Process Intensification and Green Chemistry

Essentials of Life Cycle Assessment

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Master of Science in Chemical Engineering and Biotechnology
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    - Context and general description
    - LCA methodology. Definitions, system boundaries, LCA phases.
    - Example (Palladium acetate synthesis)
- Impact categories
    - Calculation of impact potential
    - Description of some impact categories: Global warming, Ozone layer depletion, Tropospheric ozone formation, Eutrophication, Acidification, Human toxicity, Abiotic resource depletion, Land use, Ecotoxicity
- LCA examples
    - Comparing petro- and bio-based polymers
    - Assessment of competing dimethyl carbonate syntheses
    - PVC production vs recycling in China
- Roles of green chemistry and engineering in LCA
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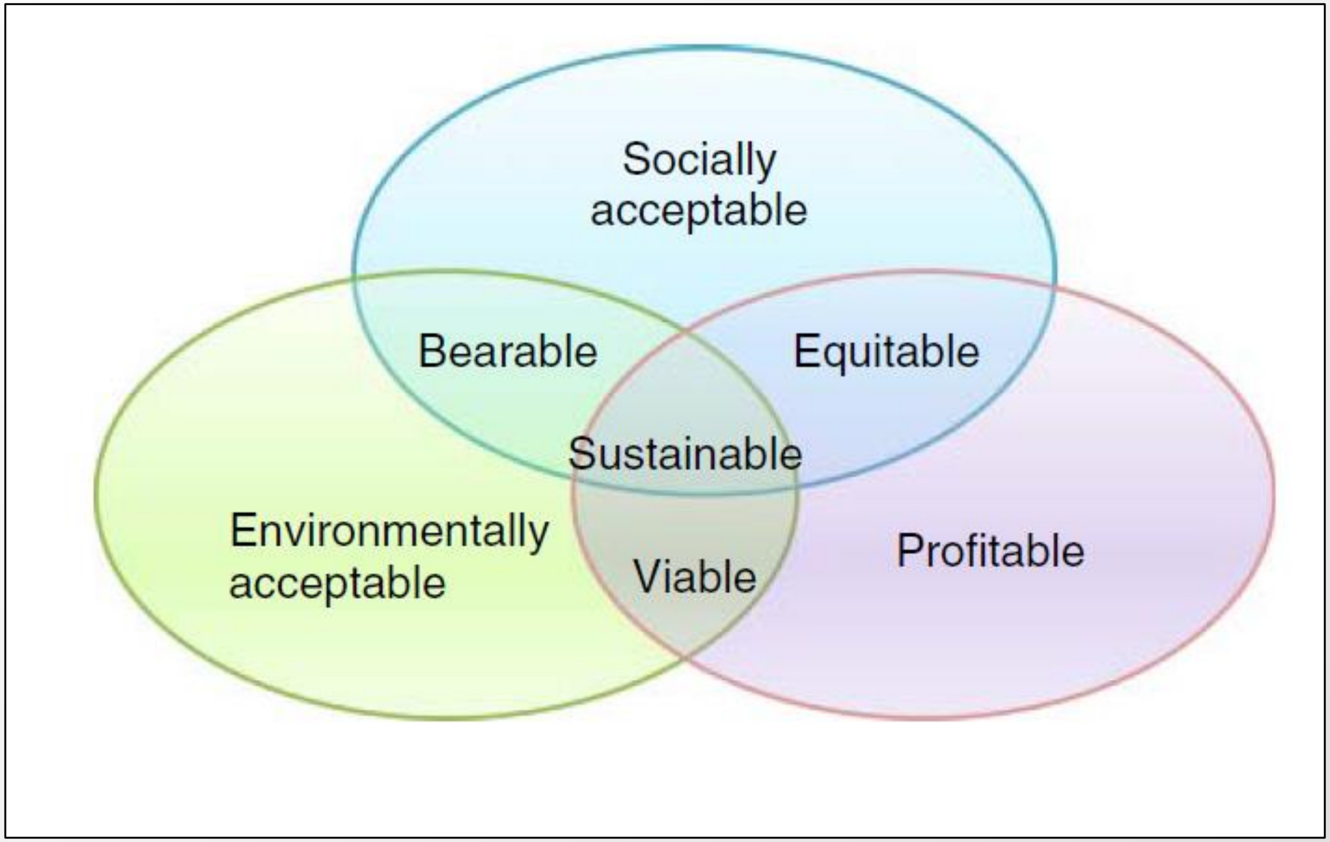
Introduction to Life Cycle Assessment

Sustainability

"Meeting the needs of current generations without sacrificing the ability to meet the needs of future generations"

Based on the 1987 Report of the World Commission on Environment and Development (Brundtland Report)

Sustainability and its various faces
Economic, social and environmental



Scale-Up of Flow Processes in the Pharmaceutical Industry by Peter Poechlauer and Wolfgang Skranc in Sustainable Flow Chemistry: Methods and Applications, First Edition. Edited by Luigi Vaccaro. 2017 Wiley-VCH.

Elements of product life cycle

Life Cycle Assessment definition*

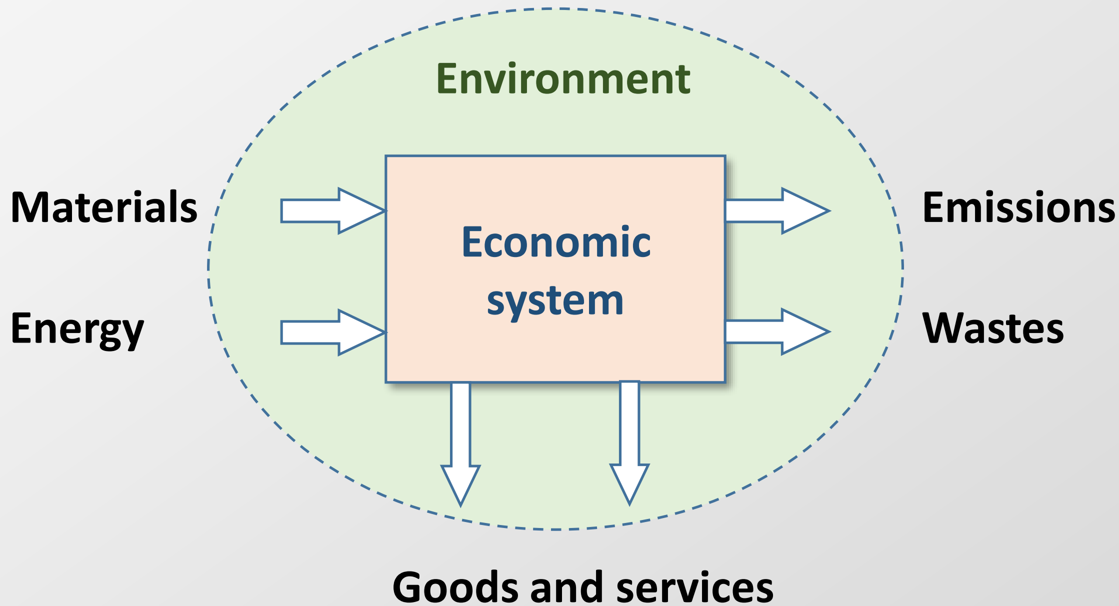
- Process to **evaluate environmental burdens** associated with a process, product or activity
- Identification and quantification of **energy** and **materials** used and **wastes** released
- Assessment of **impact** of those energy and material uses and releases to the environment
- Identify and evaluate opportunities to effect environmental **improvements**

*SETAC (Society for Environmental Toxicology and Chemistry)

LCA specifics

✓An **environmental management tool**

✓Uses a **holistic approach**: considers the environment as a whole, including indirect releases, consumption of raw materials and waste disposal



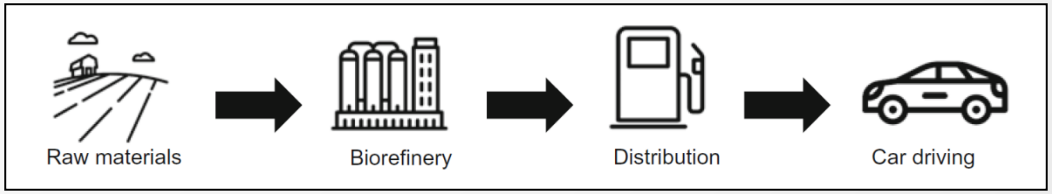
LCA specifics

- ✓**Avoids problem shifts** (“burden shifting”)
- ✓Makes the environmental impacts of different products or processes **comparable** (standardized method)
- ✓**Standardized** by DIN EN ISO 14040 and 14044

Examples of "burden shifting"

- Increasing an environmental impact while attempting to decrease another

  Example: biofuels



  - Decrease climate change impact but increase other impacts
    - Some fossil fuels required in processes prior to use stage (farming, bio-refining) → not "climate-neutral"
    - Farming → natural land (e.g. forest) loss (+release carbon bound in biomass and soil), biodiversity loss, water scarcity
    - Fertilizers → water eutrophication
    - Pesticides → toxicity on freshwater ecosystems
    - Social effects: increase of food price
- Shifting of environmental impacts from one life-cycle stage to another
- Shifting of environmental impacts from one geographical region to another

Life Cycle Assessment, Theory and Practice, 2018, Hauschild, Rosenbaum and Olsen (Eds.), Springer

LCA methodology (ISO)

Goal definition and scoping
- Define system boundaries
- **Functional unit**

Inventory analysis (LCI)
- Material and energy balances
- Identify environmental **burdens**

Impact assessment
- Aggregation of burdens into **impact categories**
- Characterization of potential impacts

Interpretation

Definitions

Functional unit of assessment

- "Quantified performance of a product system for use as a reference unit", e.g.:
  - Unit mass or volume of a product
  - Unit service delivered
  - Annual throughput of a process
  - Etc.

→ Example: what is the contribution to emissions of green house gases from manufacture of **1 t of a specific grade aluminum**?

Definitions

Burden

- The sum of emissions of a specific substance within the system's boundary

→ Example: **how many kg of CO_2** are produced to manufacture 1 t of a specific grade aluminum?

Definitions

Impact and Impact Category

- Human and environmental impacts are classified in different categories (e.g., Global warming potential, Ozone depletion potential, Photochemical ozone creation potential, …)
- All burdens (e.g., kg CO_2, kg CH_4, etc.) are used to quantify impacts, relatively to a reference substance (e.g., ethylene = reference compound for Photochemical ozone creation potential)
    - kg CO_2, kg CH_4, etc.→ kg of a single reference substance

→ Example: **how many kg of ethylene-equivalents** are emitted to produce 1 t of a specific grade aluminum?

LCA phase 1
Goal definition and scoping

Optional

Goal definition and scoping

(limits of the study)

- Goal of the study → exact definition of question, target audience and intended application
- Scope of the study → temporal, geographical and technological coverage
- Level of sophistication, definition of cut-off criteria
- Functional unit and reference flows
- System boundary

Source: Dana Kralisch, FSU Jena, 2012

LCA phase 2
Inventory analysis

Optional

Inventory analysis

(listing and categorization of elements involved in the cycle)

- Flow diagrams of the product life cycle
- Data collection and relation to unit processes
- Data estimation
- Comparability
- Definition of allocation rules for multifunctional processes
- Calculation of material and energy flows related to the functional unit
- Plausibility and validy check

LCA phase 3
Impact assessment

Optional

Impact assessment

(description and quantification of the impacts)

- **Classification**
  - Grouping of material and energy flows
  - Relation to impact categories
- **Characterisation**
  - Within each impact category
  - Transfer of mass and energy flows in specific environmental impact potentials by means of impact factors
- **Normalisation, grouping, weighting**
  - Sets the results e.g., in a national context

LCA phase 3
Impact assessment

Optional

Aims:

- ✓ Assessing the significance of potential environmental impacts
- ✓ Compressing the data obtained from the inventory analysis
- ✓ Increasing of the comparability

LCA phase "4"

Optional

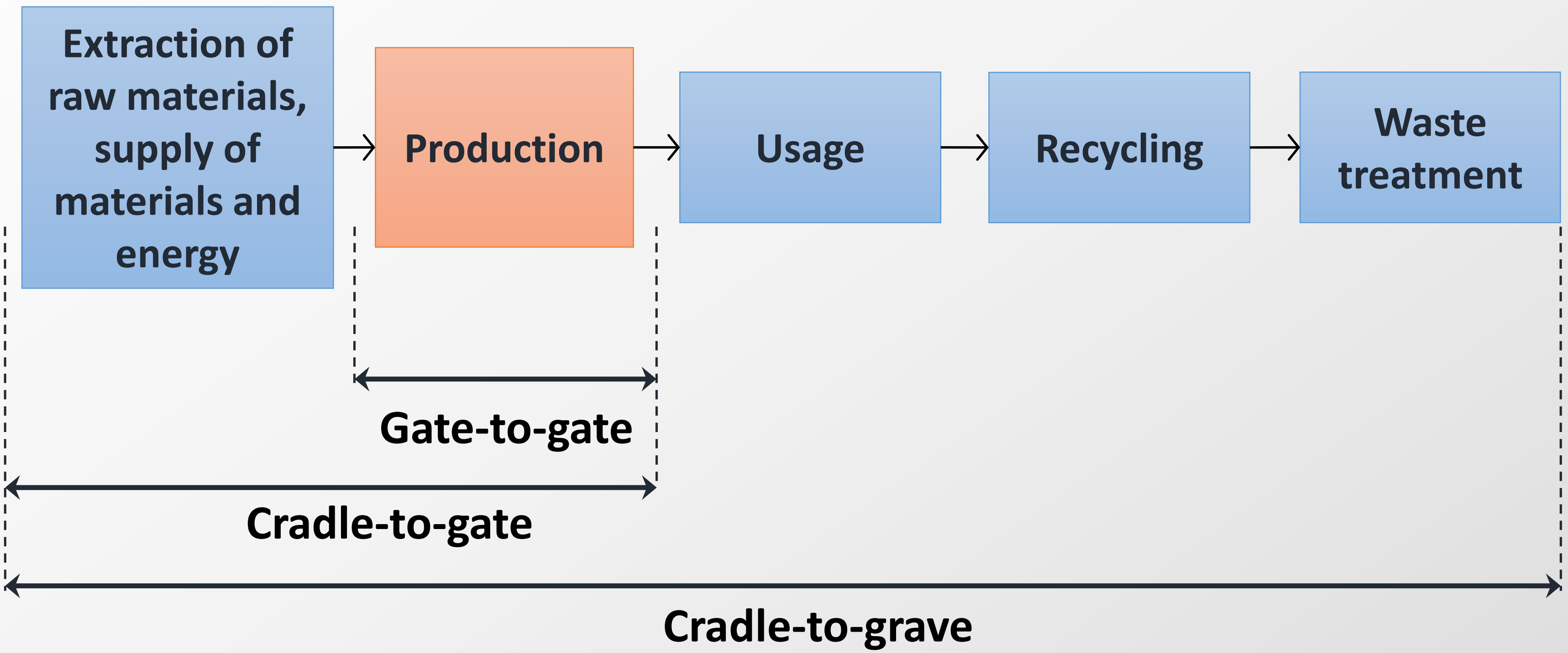
Interpretation

Aims:

✓Establish a set of conclusions

✓Make some recommendations for improvements

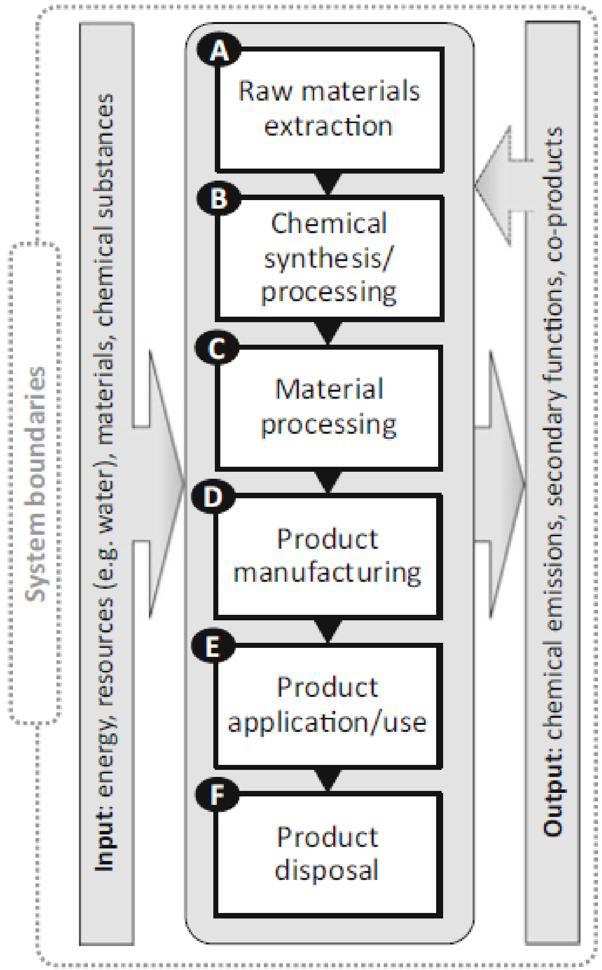
Typical system boundaries of LCA



Adapted from:
Hessel, V., D. Kralisch, and N. Kockmann, *Novel Process Windows. 2015: Wiley-VCH.*

Optional

Some relevant questions for LCA



Relevant questions for different life cycle stages…

A: Fossil or bio-based resources; virgin or recycled materials; alternative use of resource or material (e.g. food) or waste (e.g. shell or husk); location of extraction (e.g. rain forest, ocean, conflict zone); secondary functions (e.g. algae waste treatment)?

B: Reactor configuration (e.g. batch or continuous); number of reaction steps or unit operations; solvents; catalysts (e.g. enzymes, rare metals)?

C: Machine lubricants; chemical contents and concentrations?

D: Machine lubricants; solvents; adhesives?

E: Product longevity; secondary functions; exposure during use; nature of use (e.g. amount used; additional requirements such as hot water); societal function (e.g. to cure a disease)?

F: Special handling (e.g. pharmaceuticals); disposal location; process (e.g. incineration or landfil); reuse opportunity; circularity of waste streams?

A-D and **F:** Waste handling (e.g. municipal or industrial; type); co-products (e.g. materials; energy from incineration); existing or new infrastructure; efficiency; worker exploitation or occupational exposure?

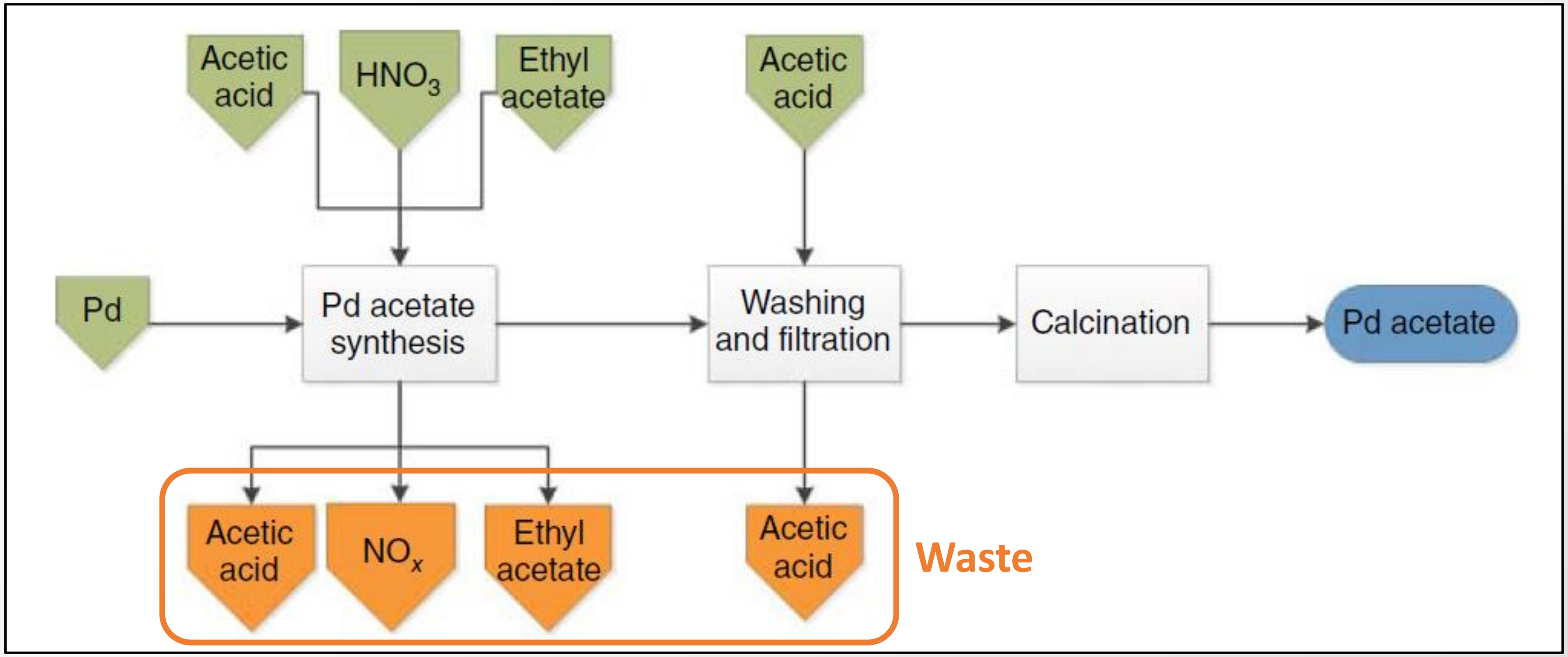
Underlined topics are mostly lacking methods or not included in environmental LCA studies

"LCA of Chemicals and Chemical Products" by P. Fantke and A. Ernstoff in: *Life Cycle Assessment, Theory and Practice, 2018, Hauschild, Rosenbaum and Olsen (Eds.), Springer*

Example: Pd acetate synthesis

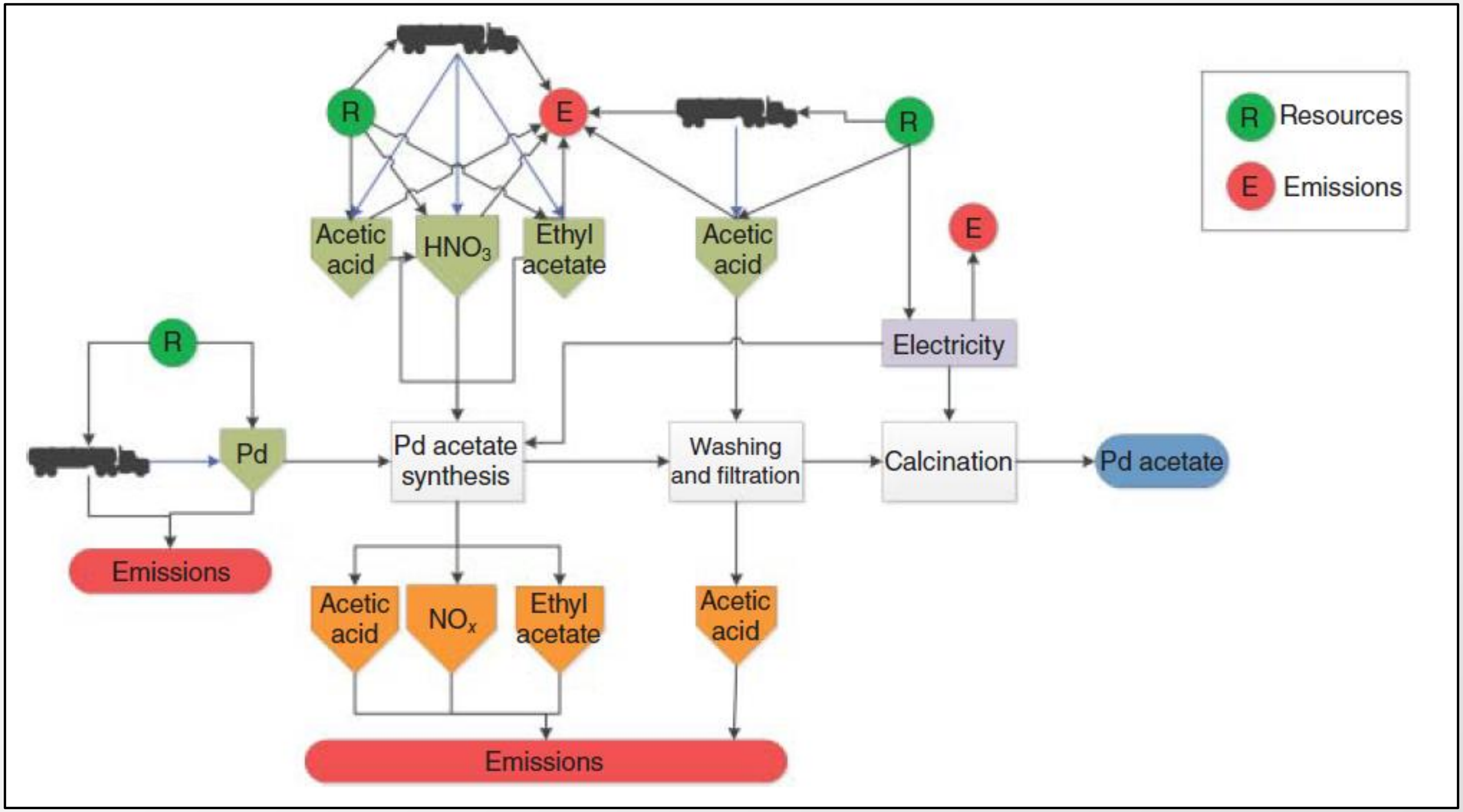
Gate-to-gate system boundary

$$3\,Pd + 6\,HNO_3 + 6\,HOAc \rightarrow Pd_3(OAc)_6 + 6\,NO_2 + 6\,H_2O$$



Alexei A. Lapkin and Polina Yaseneva, "Life Cycle Assessment of Flow Chemistry Processes", in "Sustainable Flow Chemistry Methods and Applications", Luigi Vaccaro (2017) Wiley

Example: Pd acetate synthesis
Cradle-to-gate system boundary



Alexei A. Lapkin and Polina Yaseneva, "Life Cycle Assessment of Flow Chemistry Processes", in "Sustainable Flow Chemistry Methods and Applications", Luigi Vaccaro (2017) Wiley

Example: Pd acetate synthesis
Cradle-to-gate analysis

Cradle-to-gate enables quantification of impacts on the environment of processes that lie *outside* of the immediate process of concern:

- **Manufacturing of raw materials** (Pd, AcOH, HNO_3, AcOEt)
- **Transportation of raw materials** to production site (e.g., mining of Pd-containing ore,…)
- **Energy consumption**
- **Energy mix** (e.g., prevalence of coal, gas, nuclear, or renewables in the electricity mix)

Example: Pd acetate synthesis

Cradle-to-gate analysis

Broad system boundary useful when changes in the process affect the material/energy fluxes in the upstream stages of the process/product manufacture, which in turn affect the overall environmental impact of a process and a product

Some ways of reducing environmental impact :

- Use predominantly renewable energy sources
- Reducing transportation needs by optimizing the supply chain

Example: Pd acetate synthesis

Cradle-to-grave analysis

Need to consider the process within a wider boundary in order to locate the sources of environmental impacts:

- In the process itself
- Upstream in its supply chain
- Downstream in the use phase of the product
- In its end-of-life (recycling, disposal)

Impact categories

LCA metrics

Some impact categories

- Global warming potential
- Ozone layer depletion potential
- Tropospheric ozone formation potential
- Acidification potential
- Eutrophication potential
- Smog formation potential
- Abiotic resource depletion
- Land use
- Persistence
- Bioaccumulation
- Carcinogenicity
- Ecotoxicity
- Human toxicity
  - by ingestion
  - by inhalation

Calculation of impact potential

- Takes into account the quantity of material waste & its inherent harmfulness
- For every chemical involved, a risk potential (P) is calculated relative to an equal mass of a reference compound
- The risk potential (P) is multiplied by the mass of chemical released to the environment (m) to give the risk index (I):

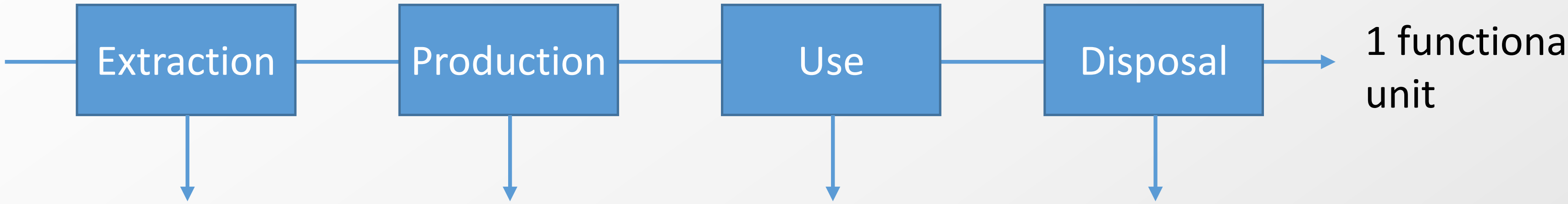
$$Risk\ index = Risk\ potential \times Mass\ of\ chemical\ released$$

Impact for single chemical released: $I = P\,m$

Total impact for n chemicals released: $I = \sum_{i=1}^{n} P_i m_i$

Calculation of impact potential

Example with only 2 emitted components (N_2O and CH_4) for a single impact category (global warming potential, GWP):



$m_{CH4,1}; m_{N2O,1}$ $\quad$ $m_{CH4,2}; m_{N2O,2}$ $\quad$ $m_{CH4,3}; m_{N2O,3}$ $\quad$ $m_{CH4,4}; m_{N2O,4}$

CH_4 burden $\quad$ N_2O burden $\quad$ GW risk potentials relative to CO_2

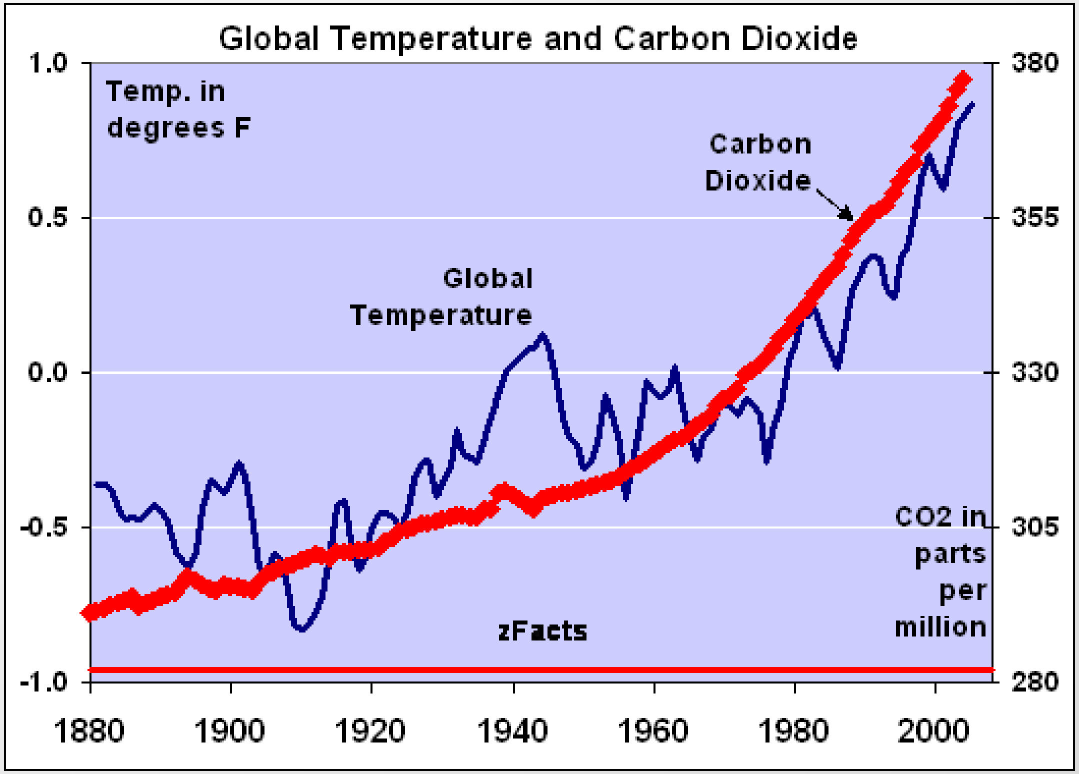
$$I_{GW} = P_{CH4,CO2} \cdot \sum_{i=1}^{4} m_{CH4,i} + P_{N2O,CO2} \cdot \sum_{i=1}^{4} m_{N2O,i} = 62 \sum_{i=1}^{4} m_{CH4,i} + 275 \sum_{i=1}^{4} m_{N2O,i}$$

CH_4 impact on global warming $\quad$ N_2O impact on global warming

Impact categories: GWP

Global Warming Potential (GWP)

- Green house gases, climate change, carbon footprint
- Reference: CO_2

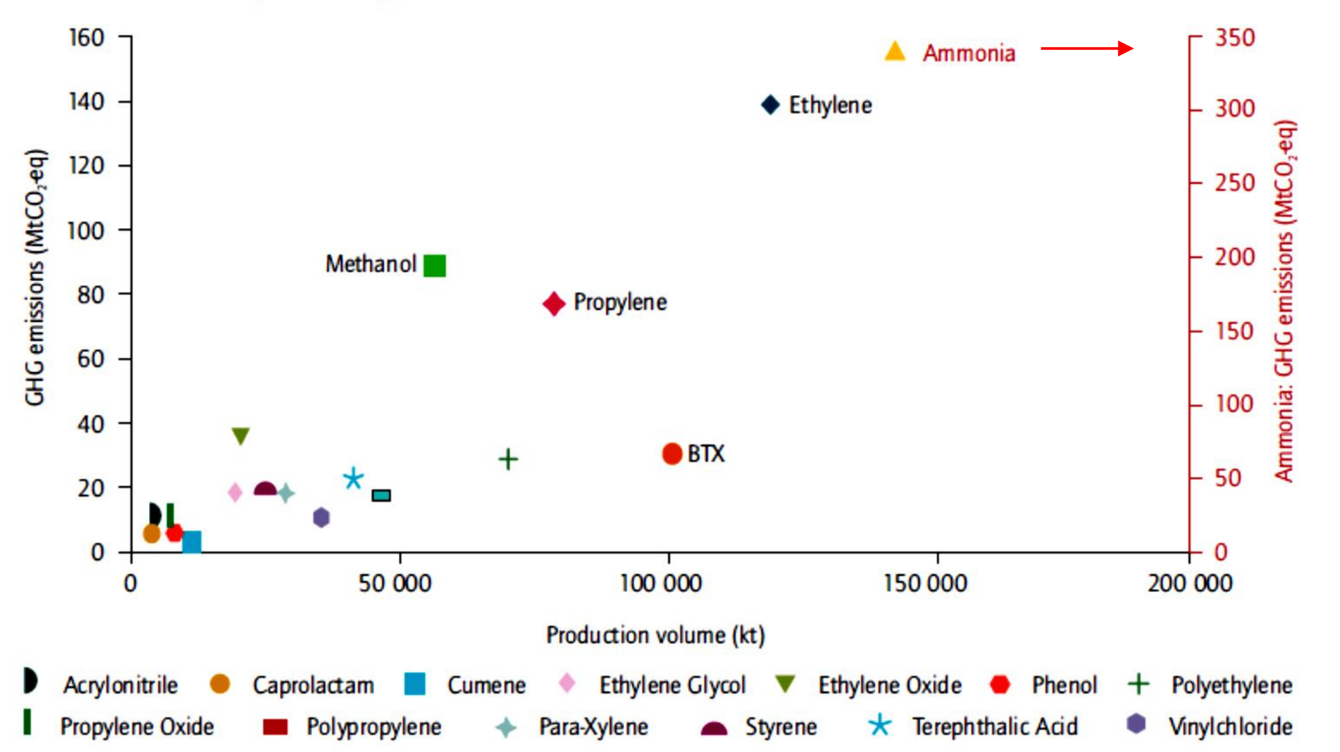


- $I_{GW} = P_{GW}\, m$
- P_{GW} values in literature

Source: Dana Kralisch, FSU Jena, 2012

Global Green House Gas (GHG) emissions versus production volumes

Top 18 large-volume chemicals (2010)



Note: GHG emissions for olefins in this figure represent that of the steam cracking process. Ammonia is presented on a different axis on the right.

GHG emissions of catalytic chemical processes are dominated by top large-volume products

Technology Roadmap, 2013, DECHEMA, ICCA, iea

Impact categories: GWP

Direct GWP of selected gases relative to CO_2

Chemical	Formula	Global Warming Potential, Time Horizon: 20 Years	100 Years	500 Years
Carbon dioxide	CO_2	1	1	1
Methane	CH_4	62	23	7
Nitrous oxide	N_2O	275	296	156
	Chlorofluorocarbons			
CFC-11	CCl_3F	6,300	4,600	1,600
CFC-12	CCl_2F_2	10,200	10,600	5,200
CFC-13	$CClF_3$	10,000	14,000	16,300
CFC-113	CCl_2FCClF_2	6,100	6,000	2,700
CFC-114	$CClF_2CClF_2$	7,500	9,800	8,700
CFC-115	CF_3CClF_2	4,900	7,200	9,900
	Hydrochlorofluorocarbons			
HCFC-21	$CHCl_2F$	700	210	65
HCFC-22	$CHClF_2$	4,800	1,700	540
HCFC-123	CF_3CHCl_2	390	120	36
HCFC-124	CF_3CHClF	2,000	620	190
HCFC-141b	CH_3CCl_2F	2,100	700	220
HCFC-142b	CH_3CClF_2	5,200	2,400	740
HCFC-225ca	$CF_3CF_2CHCl_2$	590	180	55
HCFC-225cb	$CClF_2CF_2CHClF$	2,000	620	190
	SF_6		23’500	

C. Jiménez-Gonzáles, D.J.C. Constable, 2010

Impact categories: GWP

Direct GWP of selected gases relative to CO_2

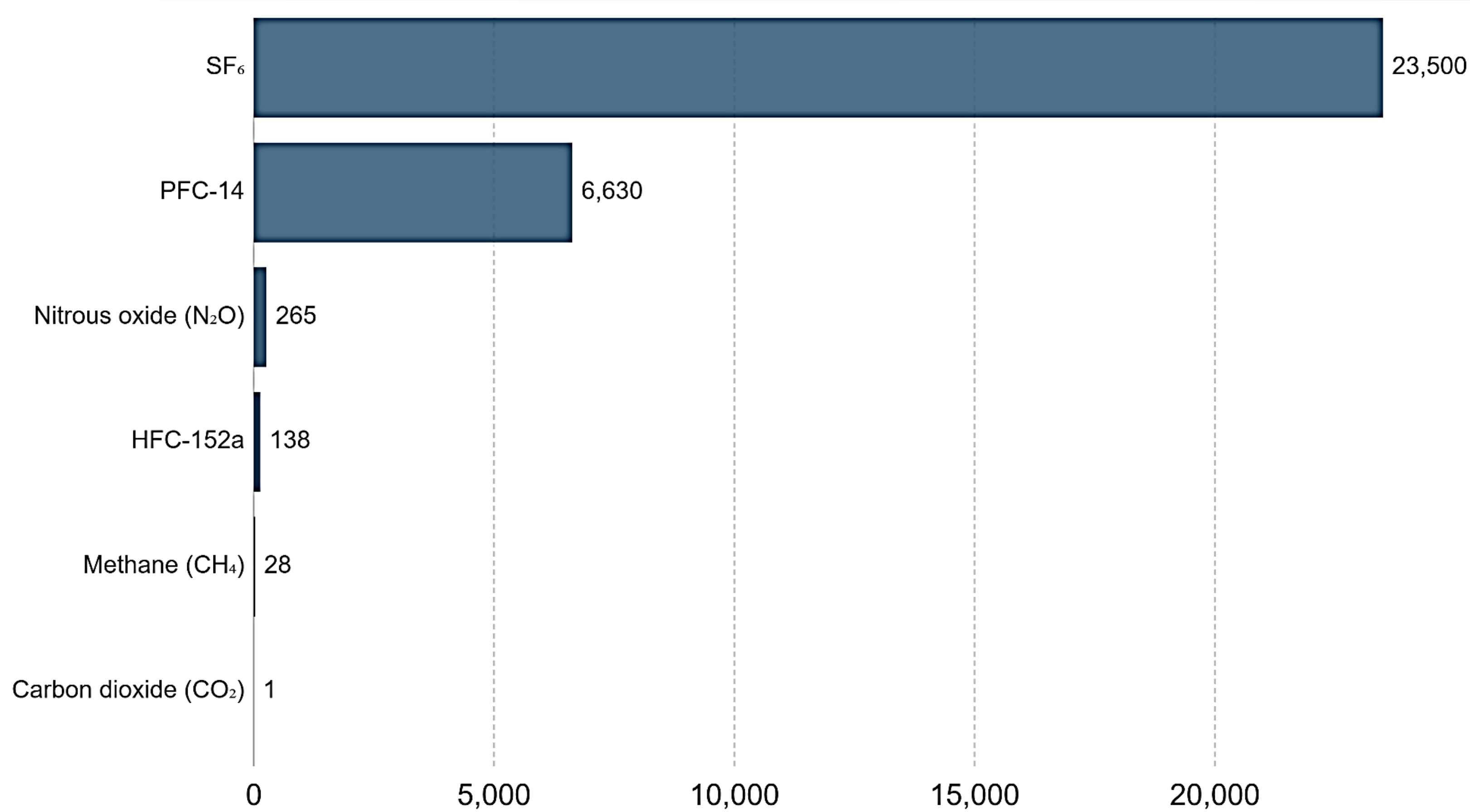
Chemical	Formula	Global Warming Potential, Time Horizon 20 Years	100 Years	500 Years
Hydrofluorocarbons				
HFC-23	CHF_3	9,400	12,000	10,000
HFC-32	CH_2F_2	1,800	550	170
HFC-41	CH_3F	330	97	30
HFC-125	CHF_2CF_3	5,900	3,400	1,100
HFC-134	CHF_2CHF_2	3,200	1,100	330
HFC-134a	CH_2FCF_3	3,300	1,300	400
HFC-143	CHF_2CH_2F	1,100	330	100
HFC-143a	CF_3CH_3	5,500	4,300	1,600
HFC-152	CH_2FCH_2F	140	43	13
HFC-152a	CH_3CHF_2	410	120	37
HFC-161	CH_3CH_2F	40	12	4
HFC-227ea	CF_3CHFCF_3	5,600	3,500	1,100
HFC-236cb	$CH_2FCF_2CF_3$	3,300	1,300	390
HFC-236ea	CHF_2CHFCF_3	3,600	1,200	390
HFC-236fa	$CF_3CH_2CF_3$	7,500	9,400	7,100
HFC-245ca	$CH_2FCF_2CHF_2$	2,100	640	200
HFC-245fa	$CHF_2CH_2CF_3$	3,000	950	300
HFC-365mfc	$CF_3CH_2CF_2CH_3$	2,600	890	280
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	3,700	1,500	470

C. Jiménez-Gonzáles, D.J.C. Constable, 2010

Optional

Impact categories: GWP

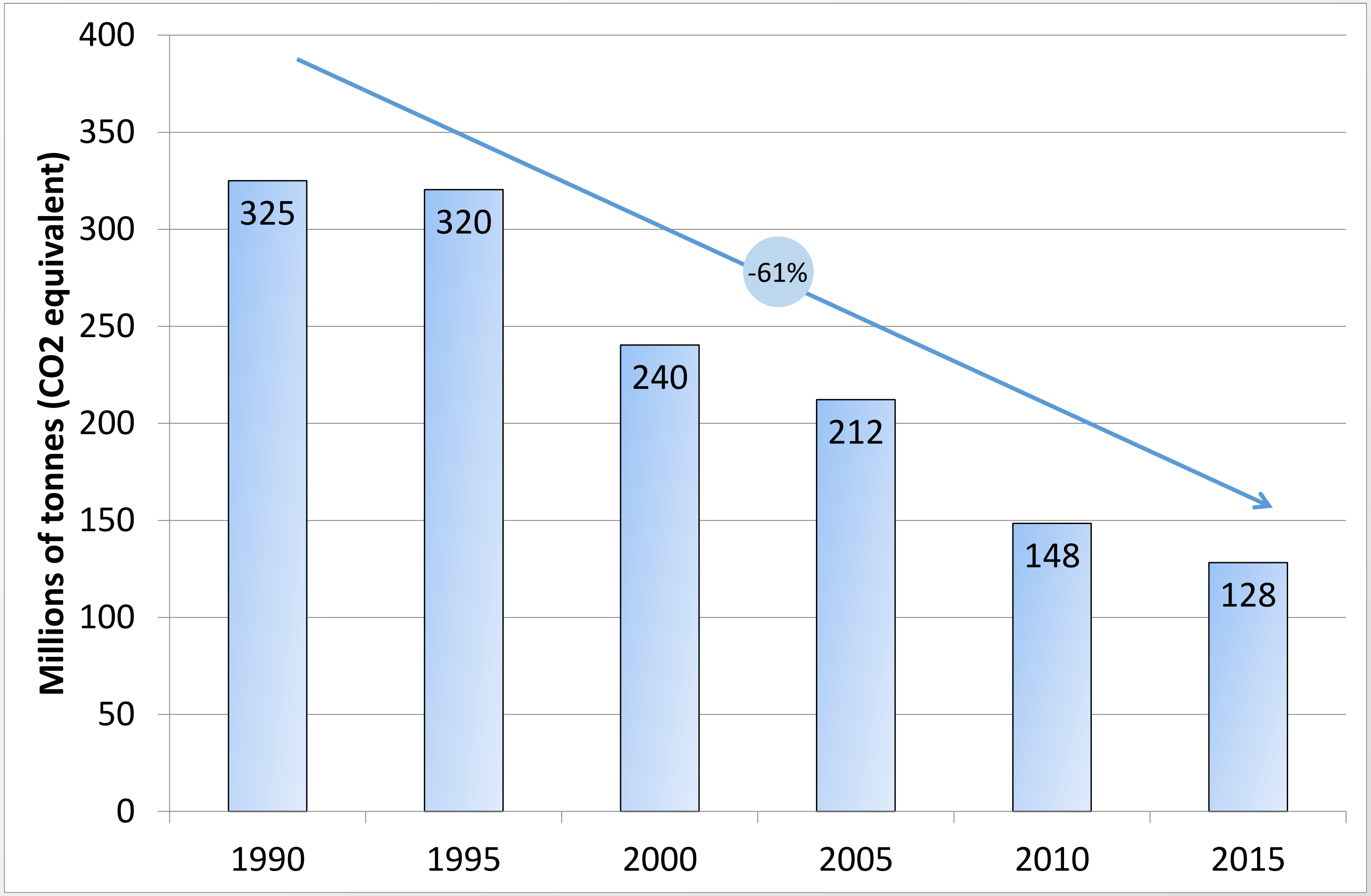
Direct GWP of selected gases over 100-yr timescale



Adapted from https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

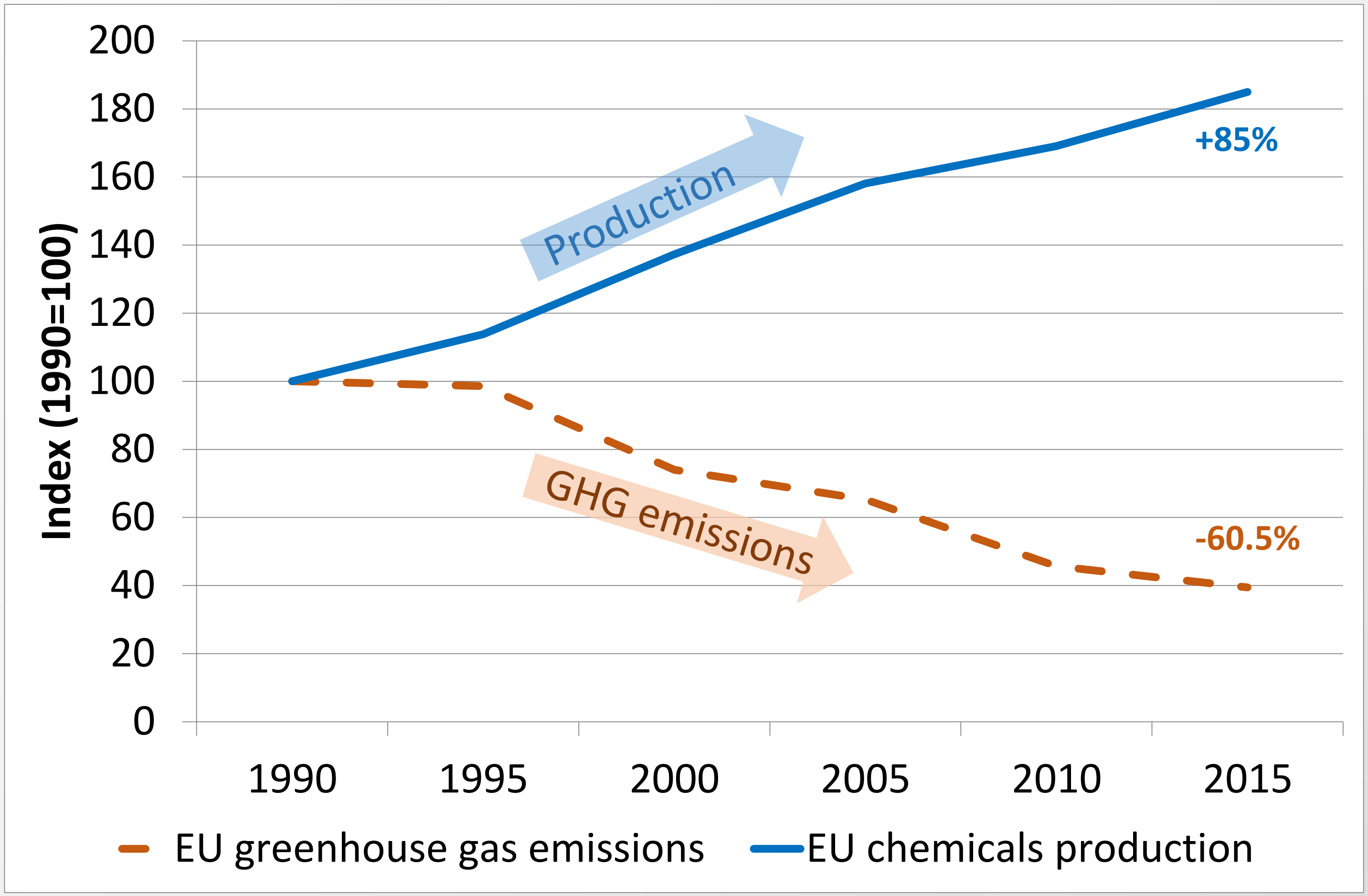
Impact categories: GWP

Total GHG emissions in the EU chemicals & pharmaceutical industry



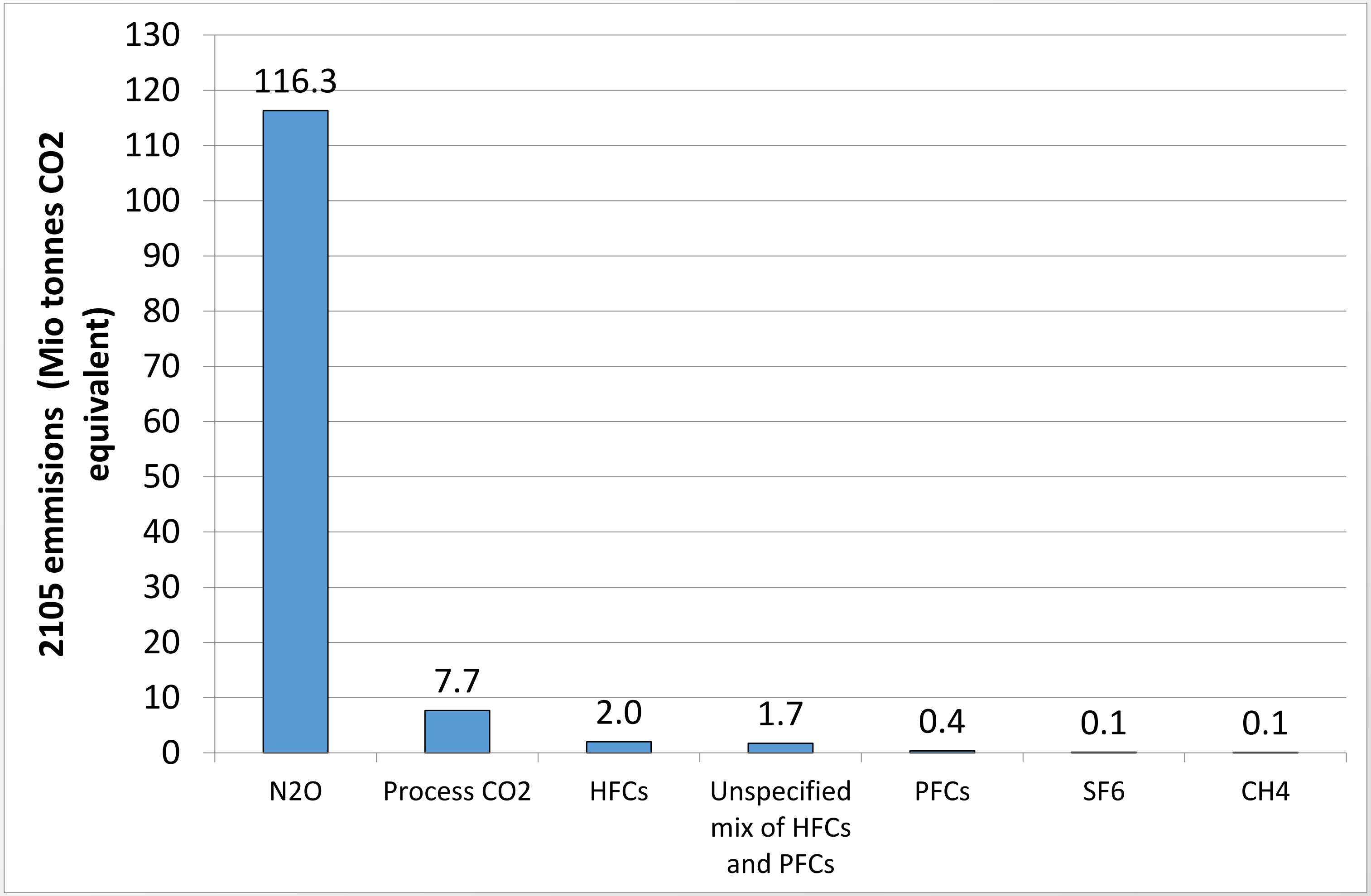
Impact categories: GWP

Production vs total GHG emissions in the EU chem. & pharma. industry



Impact categories: GWP

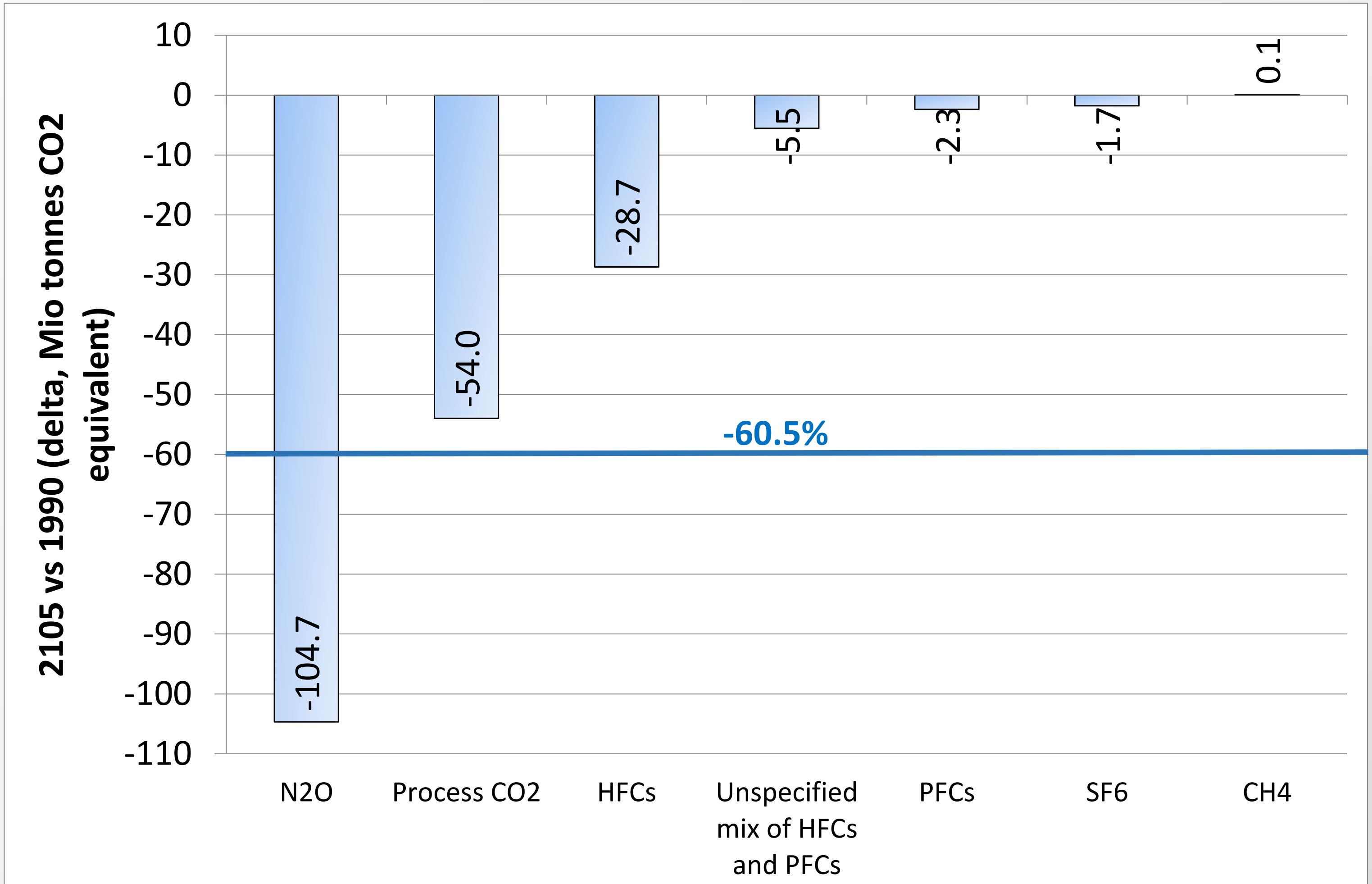
2015 EU equivalent emissions by gas in the EU chem. & pharma. industry



Impact categories: GWP

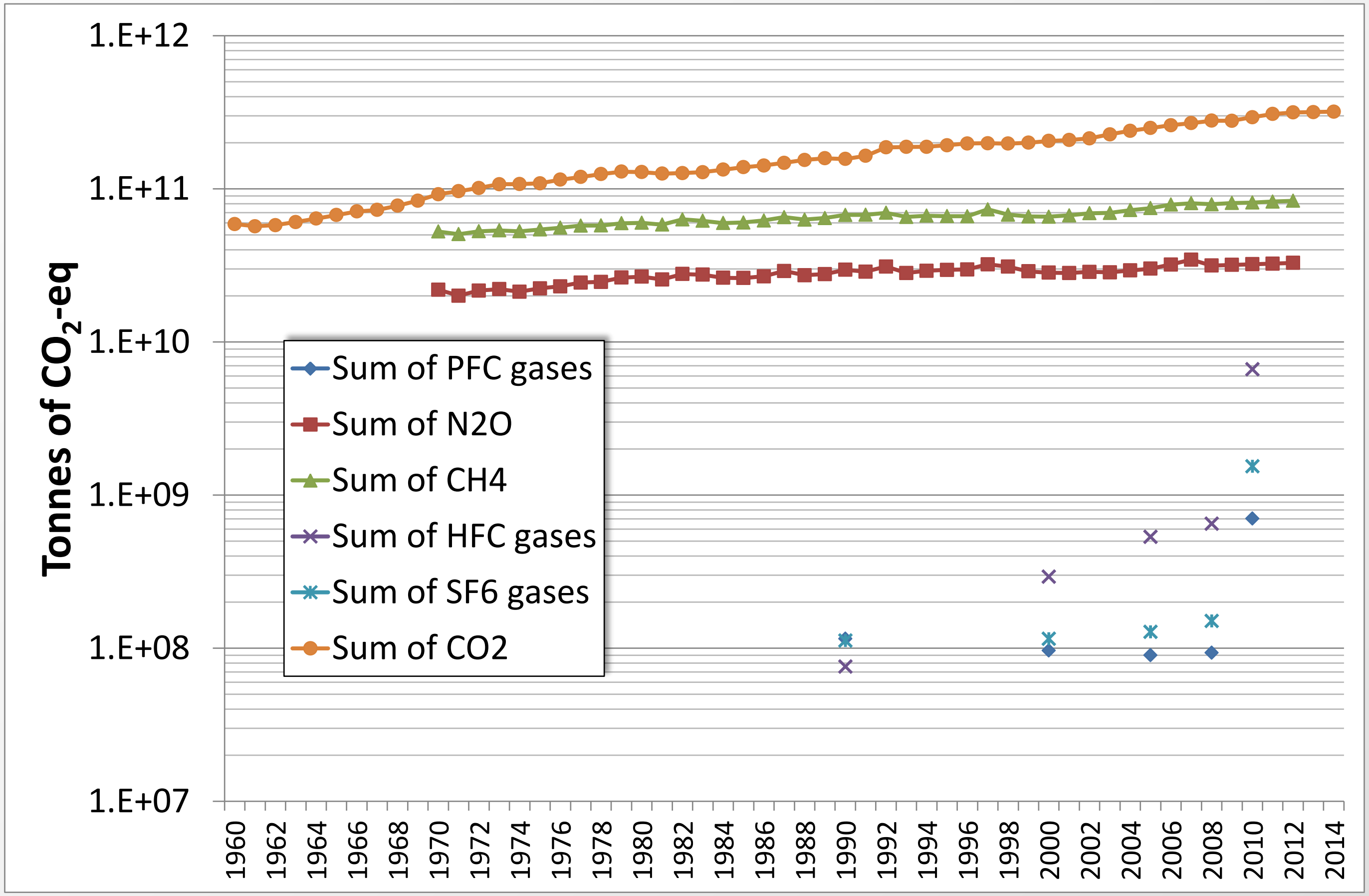
Optional

Evolution of total emissions by gas in the EU chem. & pharma. industry



Impact categories: GWP

Worldwide greenhouse gas emissions (CO2-eq)



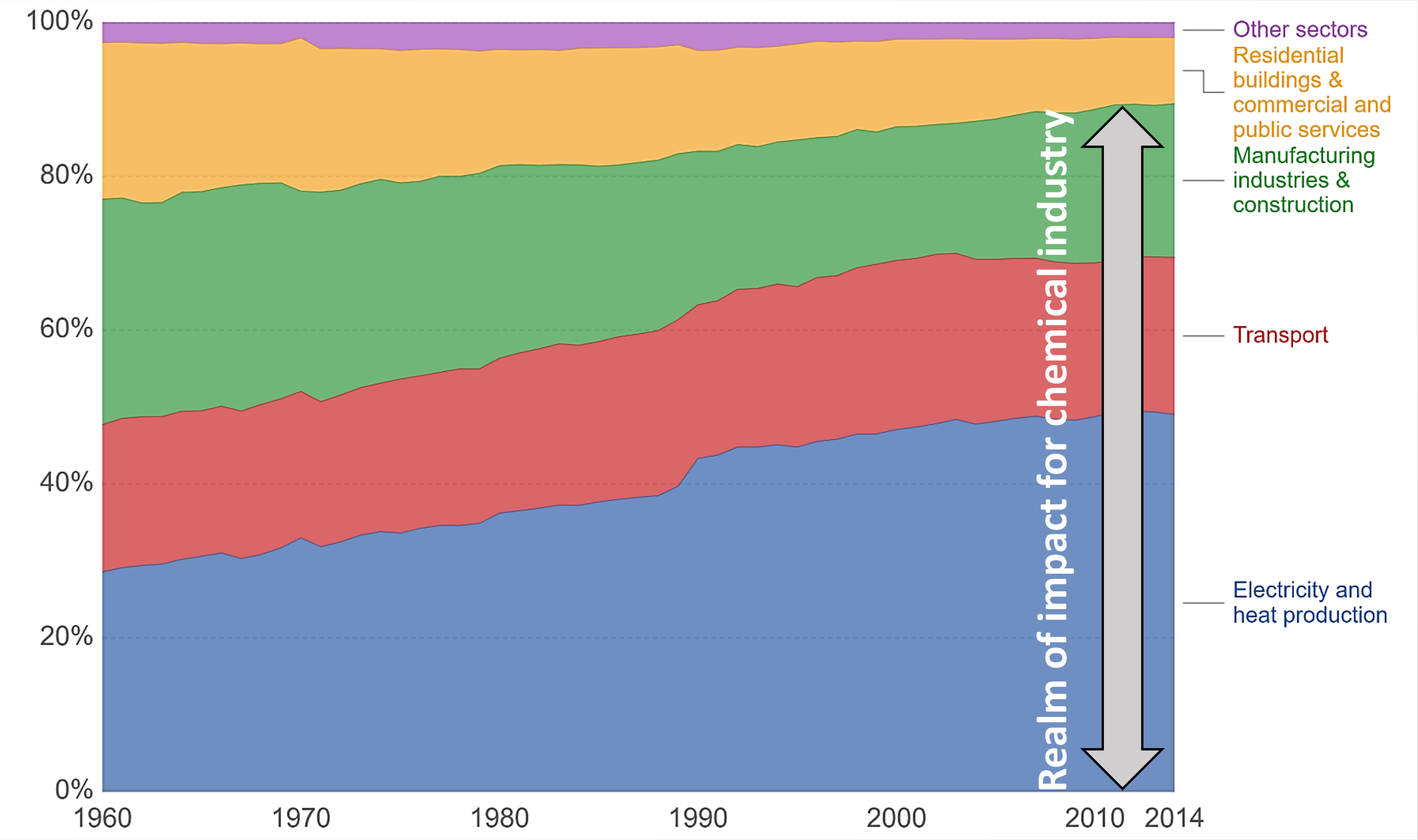
HFC: hydrofluorocarbons; PFC: perfluorocarbons

Adapted from https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

Impact categories: GWP

Optional

CO_2 emissions by sector or source



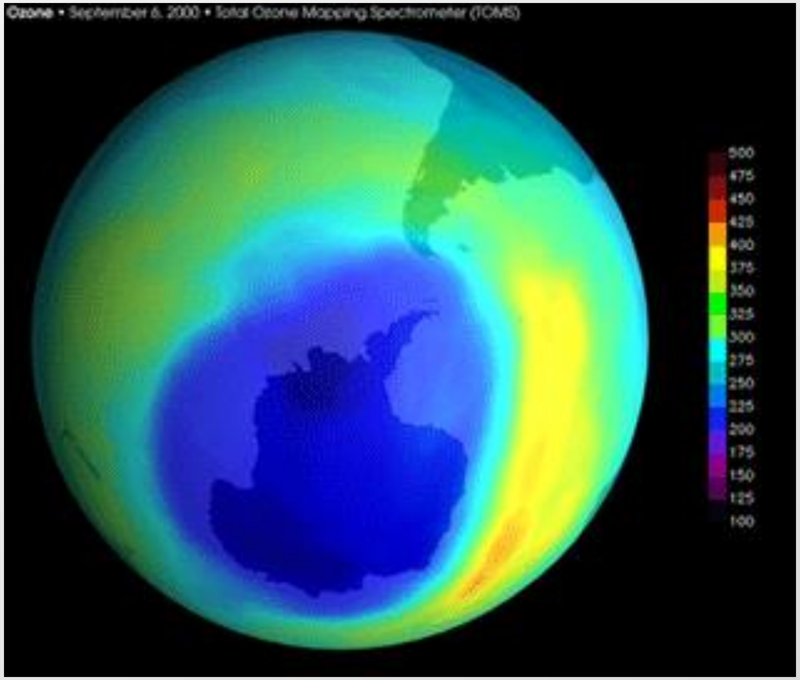
Adapted from https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

Impact categories: ODP

Ozone Depletion Potential (ODP)

- Thinning of the stratospheric ozone layer → increase of UV-B radiation
- Reference: CFC 11 (CCl_3F)

Antarctic ozone hole (2000)



- $I_{\mathrm{OD}} = P_{\mathrm{OD}}\, m$
- P_{OD} values in literature

Impact categories: ODP

Ozone depletion mechanism

Stratospheric ozone depletion by chlorine radicals

$$\text{Chlorofluorocarbons} \xrightarrow{\text{UV}} Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O_3 \longrightarrow Cl^{\bullet} + 2\ O_2$$

$$2\ O_3 \longrightarrow 3\ O_2$$

Impact categories: ODP

Ozone depletion potential of selected gases (CFC-11 equivalents)

Compound	Lifetime (years)	Ozone Depletion Potential, Montreal Protocol
Trichlorofluoromethane	45	1
Dichlorodifluoromethane	100	1
1,1,2-Trichlorotrifluoroethane	85	0.8
Dichlorotetrafluoroethane	300	1
Monochloropentafluoroethane	1700	0.6
Bromochlorodifluoromethane	16	3
Bromotrifluoromethane	65	10
Dibromotetrafluoroethane	20	6
Chlorotrifluoromethane	640	1
Pentachlorofluoroethane	—	1
Tetrachlorodifluoroethane	—	1
Heptachlorofluoropropane	—	1
Hexachlorodifluoropropane	—	1
Pentachlorotrifluoropropane	—	1
Tetrachlorotetrafluoropropane	—	1
Trichloropentafluoropropane	—	1
Dichlorohexafluoropropane	—	1
Chloroheptafluoropropane	—	1
Carbon tetrachloride	26	1.1
N_2O		0.017

Impact categories: POCP

Photochemical Ozone Creation Potential (POCP)

- Summer smog, photo-oxidant formation in the troposphere
- Reference: C_2H_4

Impact categories: POCP
Ozone formation mechanism

Photochemical ozone formation (partial mechanism)
Involves hydrocarbon radicals and NO

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + NO \longrightarrow NO_2 + RO^{\bullet}$$

$$NO_2 \xrightarrow{\text{light}} NO + O$$

$$O + O_2 \longrightarrow O_3$$

Impact categories: POCP

Photochemical ozone creation potential values of selected compounds

Compound	POCP 100 kg ethylene equivalents
Alkanes	
Methane	3.4
Ethane	14
Propane	41.1
n-Butane	59.9
i-Butane	42.6
n-Pentane	62.4
i-Pentane	59.8
n-Hexane	64.8
2-Methylpentane	77.8
3-Methylpentane	66.1
2,2-Dimethylbutane	32.1
2,3-Dimethylbutane	94.3
n-Heptane	77
2-Methylhexane	71.9
3-Methylhexane	73
n-Octane	68.2
2-Methylheptane	69.4
n-Nonane	69.3
2-Methyloctane	70.6
n-Decane	68
2-Methylnonane	65.7
n-Undecane	61.6
n-Dodecane	57.7
Cyclohexane	59.5
Methylcyclohexane	73.2
Ethylene (reference)	**100**

C. Jiménez-Gonzáles, D.J.C. Constable, 2010

Impact categories: EP

Eutrophication Potential (EP)

- Nutrient enrichement in aquatic and terrestrial ecosystems causing excessive growth of plants and algae
- Reference: PO_4^{3-} / NO_x

Freshwater (→ PO_4^{3-}) Marine (→ NO_x)

Impact categories: EP

Substance	Eutrophication potential (in kg PO_4^{3-} eq./kg)
Ammonia	0.35
Ammonium	0.33
Nitrate	0.1
Nitric acid	0.1
Nitrogen	0.42
Nitrogen dioxide	0.13
Nitrogen monoxide	0.2
Nitrogen oxides	0.13
Phosphate	1
Phosphoric acid (H_3PO_4)	0.97
Phosphorus (P)	3.06
Phosphorus (V) oxide (P_2O_5)	1.34

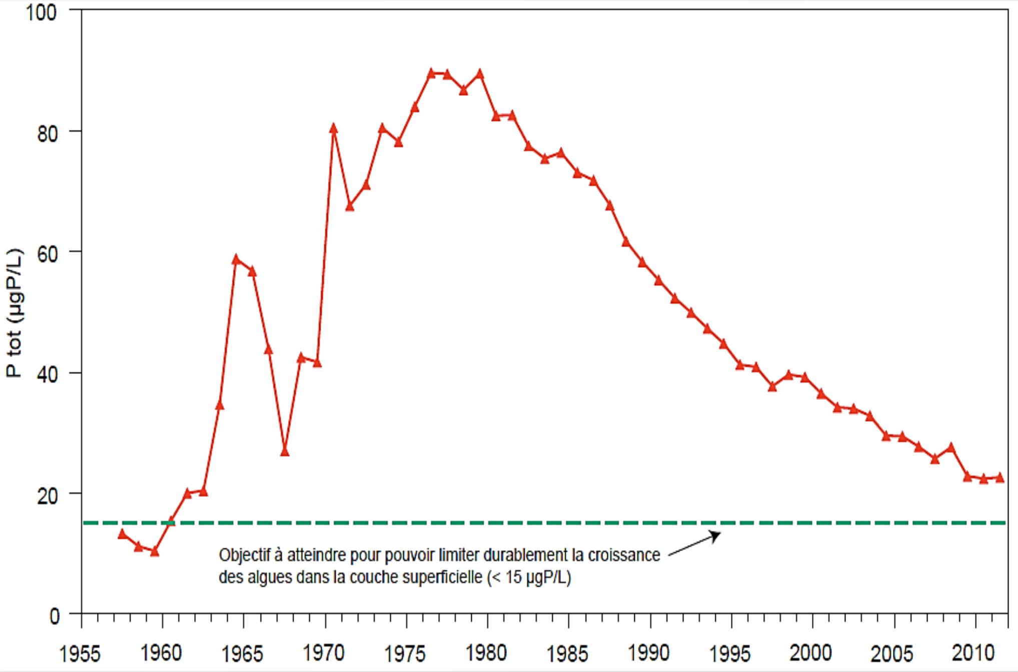
Impact categories: EP

Mean annual concentration of P in Geneva Lake

- Lake Geneva: the largest and deepest lake in Western Europe
- Supplies more than 600'000 people with drinking water
- 1950: deterioration of its health, sharp increase in P with a peak in 1979 (89.5 µgP/L)

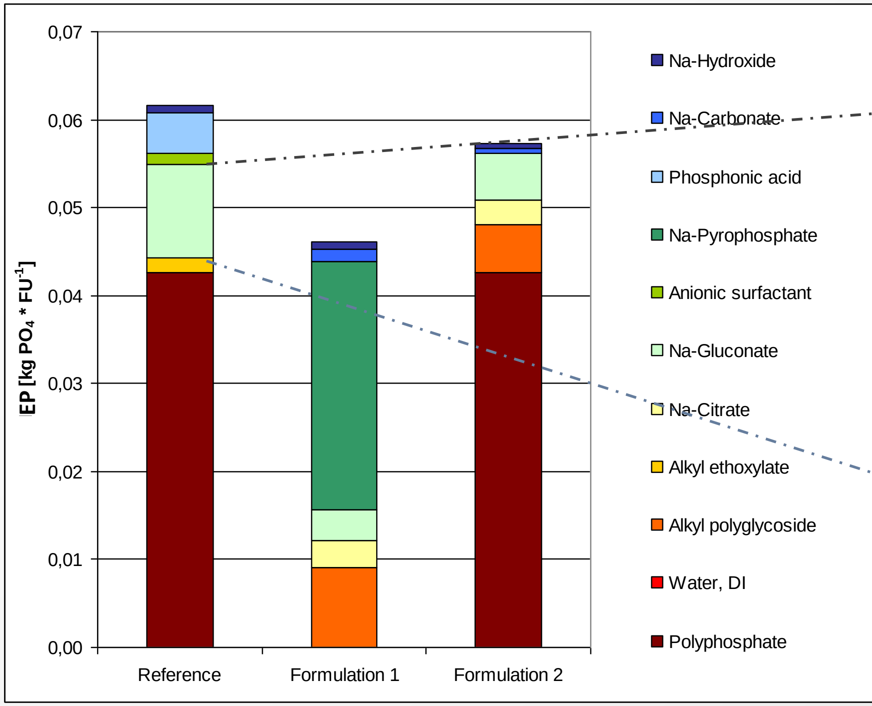
Actions undertaken (CH & FR):

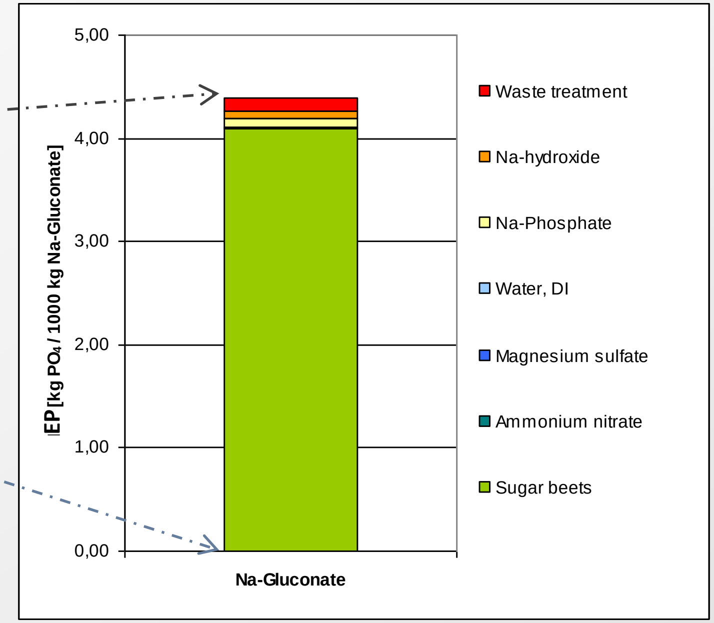
- Increase of wastewater treatment plants eliminating P
- Ban on P in laundry products
- Improving the quality of sewerage networks (limitation of sewer overflows)
- Actions in agriculture to reduce P fertilization



Rapin and Gerdeaux, Arch.Sci. (2013) 66 : 103-116

Impact categories: EP
Comparison of 3 industrial cleaners





Source: Kralisch, FSU Jena

- Main impact: supply of phosphates
- Supply of alkyl polyglycoside less relevant, but higher impact than alkyl ethoxylate + anionic surfactant
- EP of Na-gluconate (and also citrate) is dominated by the cultivation of sugar beets (raw material of the fermentative gluconate production)

Impact categories: AP

Acidification Potential (AP)

- Acid rain, forest decline, fish mortality, crumbling of building materials
- Reference: SO_2

- $I_{\mathrm{AP}} = P_{\mathrm{AP}}\, m$
- $P_{AP} = \frac{\alpha}{MW} \frac{MW_{SO_2}}{\alpha_{SO_2}} = \frac{\alpha}{MW} \frac{64.1}{2}$
- α = no of dissociable protons; MW = mol. weight
- P_{AP} for many gaseous compounds in literature

Mercer et al., J. Chem. Educ. 2012, 89, 215–220

Impact categories: AP

Substance	CAS number	Acidification potential in kg SO_2 equivalent
Ammonia	7664-41-7	1.6
Nitrogen oxides (as NO_2)	10102-44-0	0.5

Impact categories: HTP

Human toxicity potential (HTP)

- Impacts on human health of toxic substances from emissions of toxic substances to the air, water and soil. Human health risk of exposure on workplace excluded.
- Reference: toluene
- Two categories
  - INGTP: toxicity by ingestion
  - INHTP: toxicity by inhalation

Impact categories: HTP

Human toxicity by ingestion (INGTP)

- $I_{\text{INGT}} = P_{\text{INGT}}\, m$
- $P_{\text{INGT}} = \frac{c_W}{LD_{50}} \frac{LD_{50,tol}}{c_{W,tol}}$

c_W (final conc. of emitted substance in water) calculated with an emission model

Human toxicity by inhalation (INHTP)

- $I_{\text{INHT}} = P_{\text{INHT}}\, m$
- $P_{\text{INHT}} = \frac{c_a}{LC_{50}} \frac{LC_{50,tol}}{c_{a,tol}}$

c_a (final conc. of emitted substance in air) calculated with an emission model

Mercer et al., J. Chem. Educ. 2012, 89, 215–220

Impact categories: HTP

HTP of various air pollutants relative to toluene

Chemical Name	CAS No	RfC (mg/m3)	Residence time air (d)	**HTP**
Carbon monoxide	630-08-0	10.5	40	0.27
Hydrogen fluoride	7664-39-3	0.03	3	7.1
hydrochloric acid	7674-01-0	0.009	3	24
Ozone	10028-15-6	0.16	10	4.4
PM10		0.05	2	2.9
PM2.5		0.015	7	33
ammonia	7664-41-7	0.03	3.3	7.5
nitric acid	7697-37-2	0.04	0.12	4.2
phosphoric acid	7664-38-2	0.007	3	31
sulfate		0.025	3.3	9.8
SO2	7446-09-5	0.08	1.5	6.0
NO2	10102-44-0	0.1	0.5	4.3

RfC: reference concentration (EPA)

Hertwich et al., An update on the human toxicity potential with special consideration of conventional air pollutants, NTNU, 2006

Impact categories: ADP

Abiotic resource depletion potential (ADP)

- Extraction of minerals and fossil fuels, depletion of ultimate reserve in relation to annual use
- Reference: Sb

- $I_{\mathrm{AD}} = P_{\mathrm{AD}}\, m$
- P_{AD} values in literature

Mass used in process, not mass emitted!

Impact categories: land use

Land use

- Land competition (loss of biodiversity and loss of life support function excluded)
- Reference: $m^2 \cdot yr$

Impact categories: TETP

Ecotoxicity potential (TETP)

- Impacts of aquatic, terrestrial, sediment ecosystems
- Reference: 1,4-dichlorobenzene

Impact categories that SHALL be included in the LCA*

Optional

Impact category	Unit
Global warming	kg CO_2 eq.
Photochemical ozone formation	kg ethylene eq.
Air acidification	mol H^+ eq.
Resource depletion (fossil fuels)	kg Sb eq.
Abiotic depletion (element)	kg Sb eq.
Eutrophication (freshweater)	kg P eq.
Eutrophication (marine)	kg N eq.
Human toxicity	CTUh (comparative toxic unit for humans)
Ecotoxicity	CTUe (comparative toxic unit for ecosystems)

Life Cycle Metrics for Chemical Products (2014), Cefic guidelines (European Chemical Industry Council)

Impact categories that SHOULD be included in the LCA*

Optional

Impact category	Unit
Dust & particulate matter	kg PM2.5 eq.
Land use	kg C*yr
Species richness	m^2*yr

Life Cycle Metrics for Chemical Products (2014), Cefic guidelines (European Chemical Industry Council)

Impact categories that MAY be included in the LCA*

Optional

Impact category	Unit
Ozone depletion	kg CFC-11 eq.
Water scarcity / water availability footprint	m3 eq.

Life Cycle Metrics for Chemical Products (2014), Cefic guidelines (European Chemical Industry Council)

Energy flows that SHALL be included in the LCA*

Optional

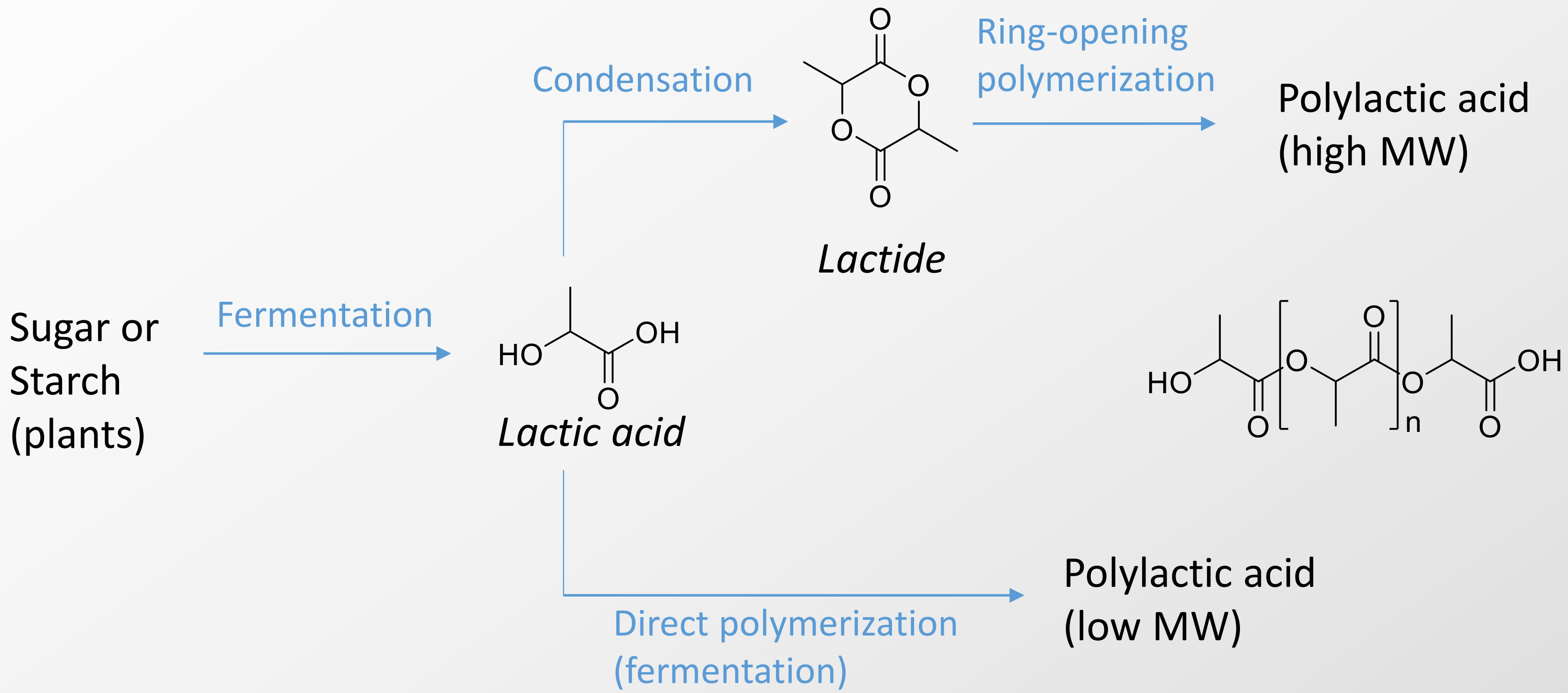
Impact category	Unit
Cumulative energy demand	MJ
Renewable energy consumption	MJ
Non-renewable energy consumption	MJ

Life Cycle Metrics for Chemical Products (2014), Cefic guidelines (European Chemical Industry Council)

LCA example

Comparing petro- and bio-based polymers

Polylactic acid synthsesis

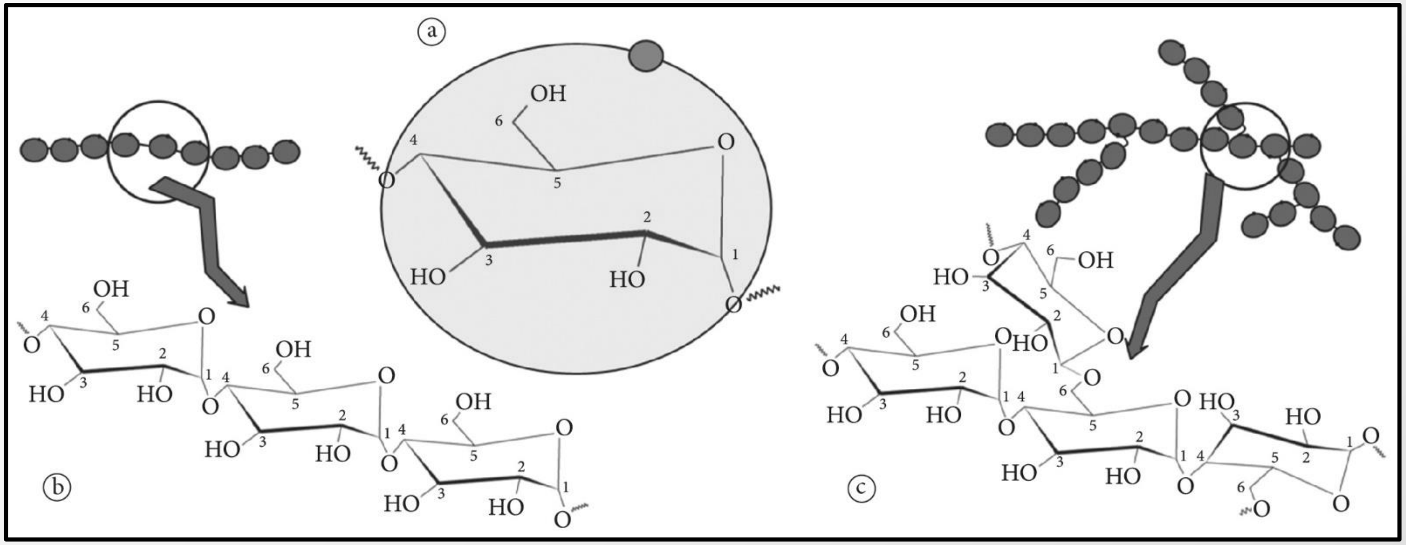


Thermoplastic starch synthesis

Heat
Shear
Plasticizers

Starch (corn, cereals, …) → Thermoplastic starch (TPS)

Starch structure

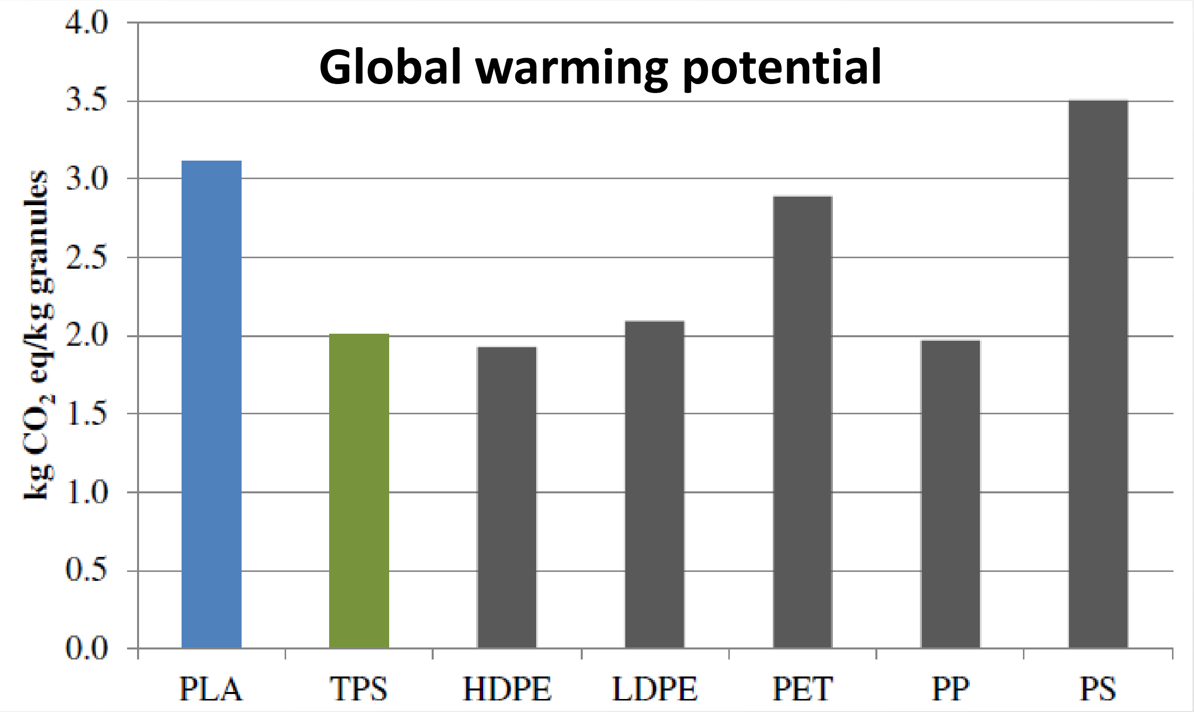


(a) glucose units, (b) amylose and (c) amylopectin

Alcázar-Alay, Sylvia Carolina, & Meireles, Maria Angela Almeida. (2015). Physicochemical properties, modifications and applications of starches from different botanical sources. *Food Science and Technology*, *35*(2), 215-236.

Life-cycle impacts of petro- vs bio-based polymers: cradle-to granule (gate)

PLA: Polylactic acid; TPS: Thermoplastic starch



Hottle, T.A., Bilec, M.M., Landis, A.E.: Sustainability assessments of bio-based polymers. Polym. Degrad. Stab. 98, 1898–1907 (2013)

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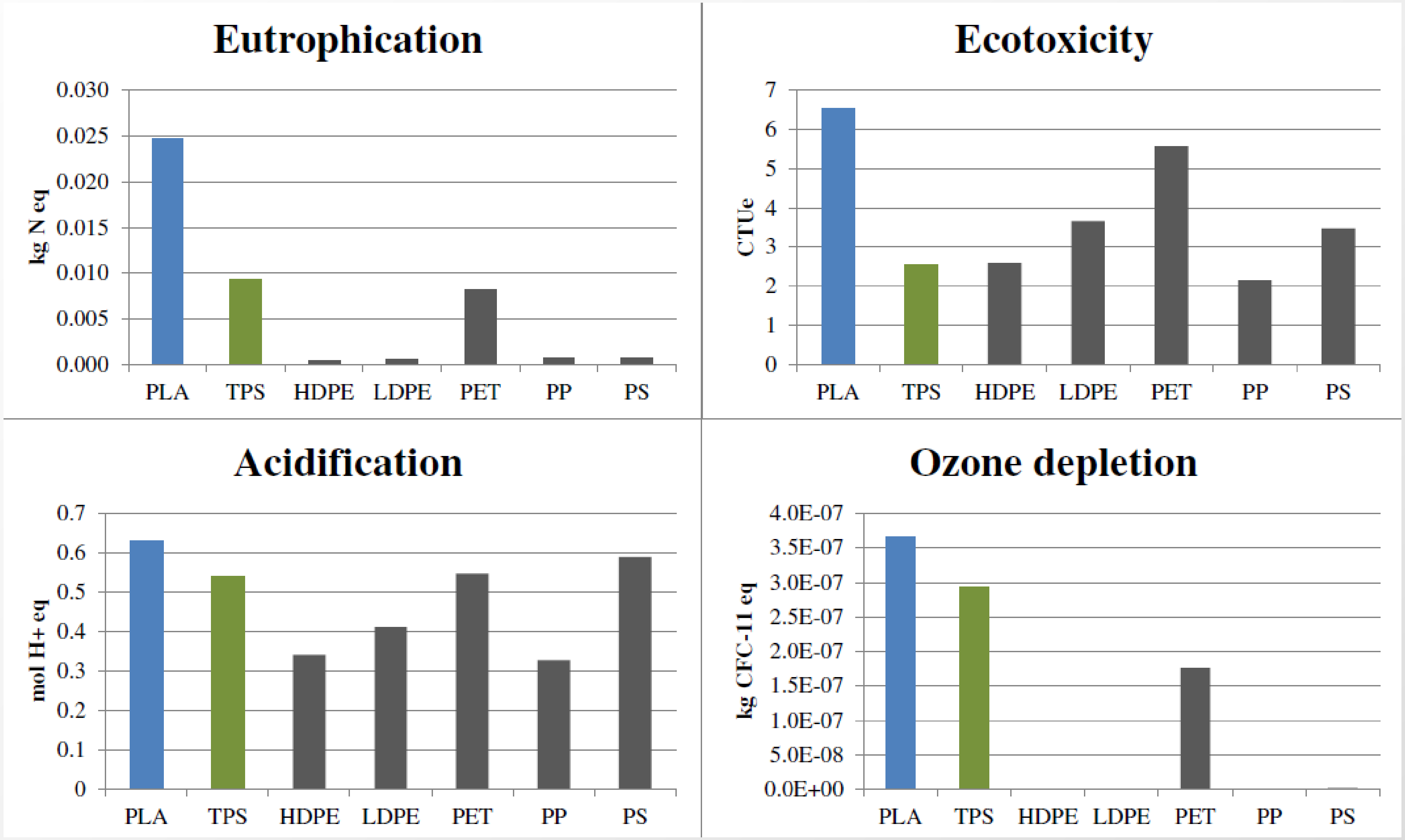

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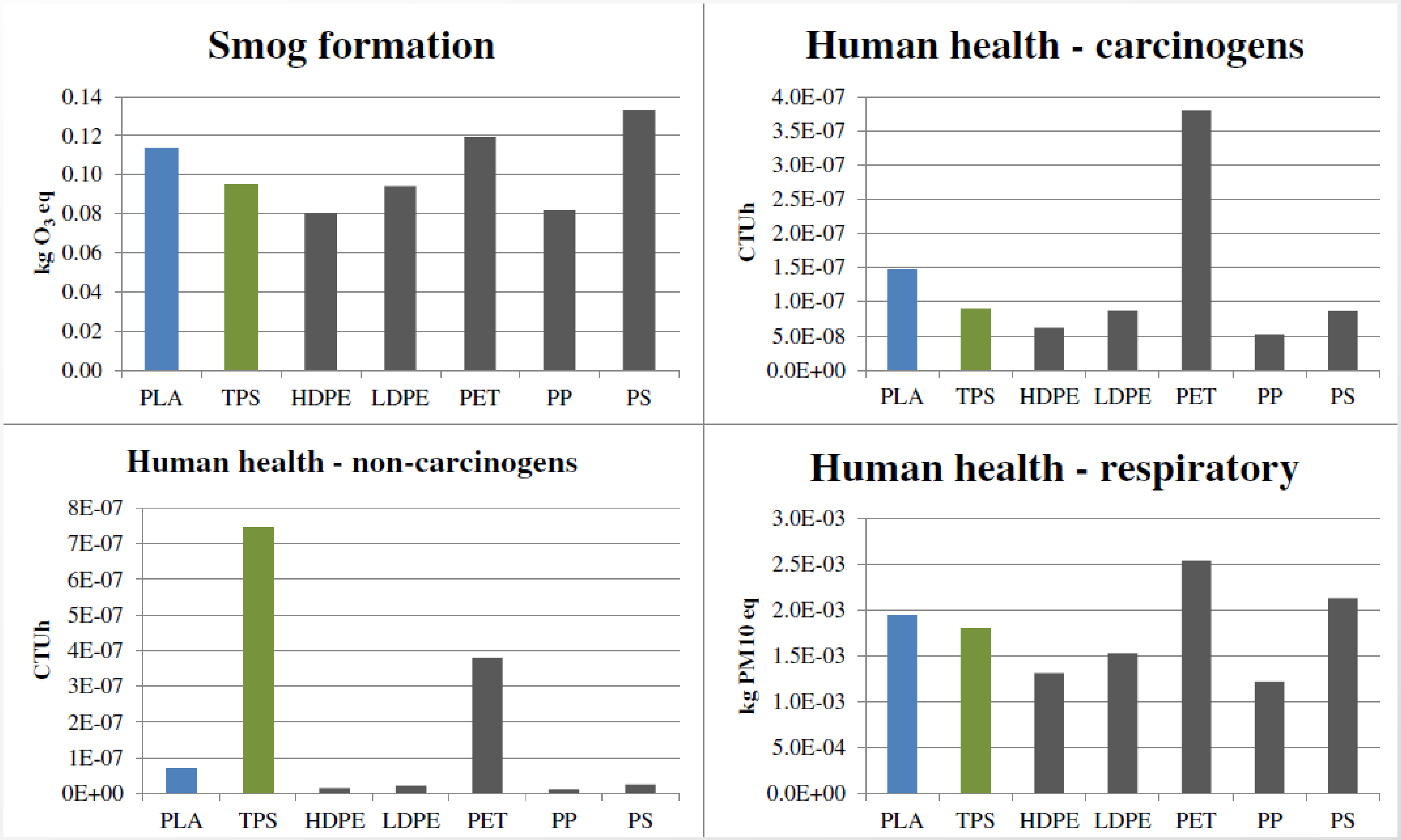

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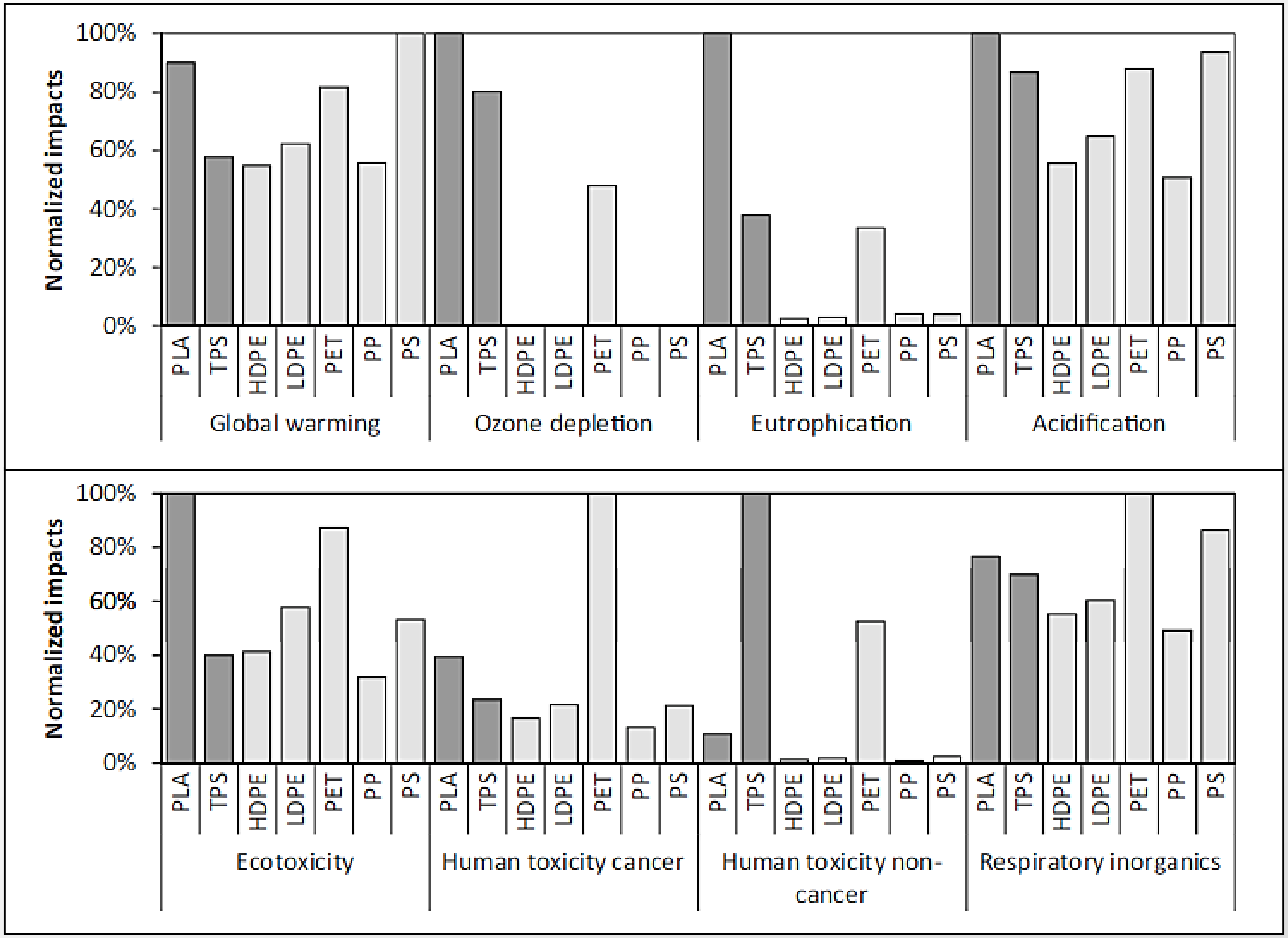


"LCA of Chemicals and Chemical Products" by P. Fantke and A. Ernstoff in: *Life Cycle Assessment, Theory and Practice, 2018, Hauschild, Rosenbaum and Olsen (Eds.), Springer*

Life-cycle impacts of petro- vs bio-based polymers

- Higher impacts of Bio-based polymers mainly due to
  - Feedstock-related agricultural emissions of fertilizers (eutrophication) and pesticides (human toxicity and ecotoxicity)
  - Deforestation (impacts related to changes in land use)

Materials and products guided by principles of ‘sustainability’, ‘eco-friendliness’ or ‘green chemistry’ can have significant, but often disregarded or unassessed, environmental impacts!

“LCA of Chemicals and Chemical Products” by P. Fantke and A. Ernstoff in: *Life Cycle Assessment, Theory and Practice, 2018, Hauschild, Rosenbaum and Olsen (Eds.), Springer*

LCA example

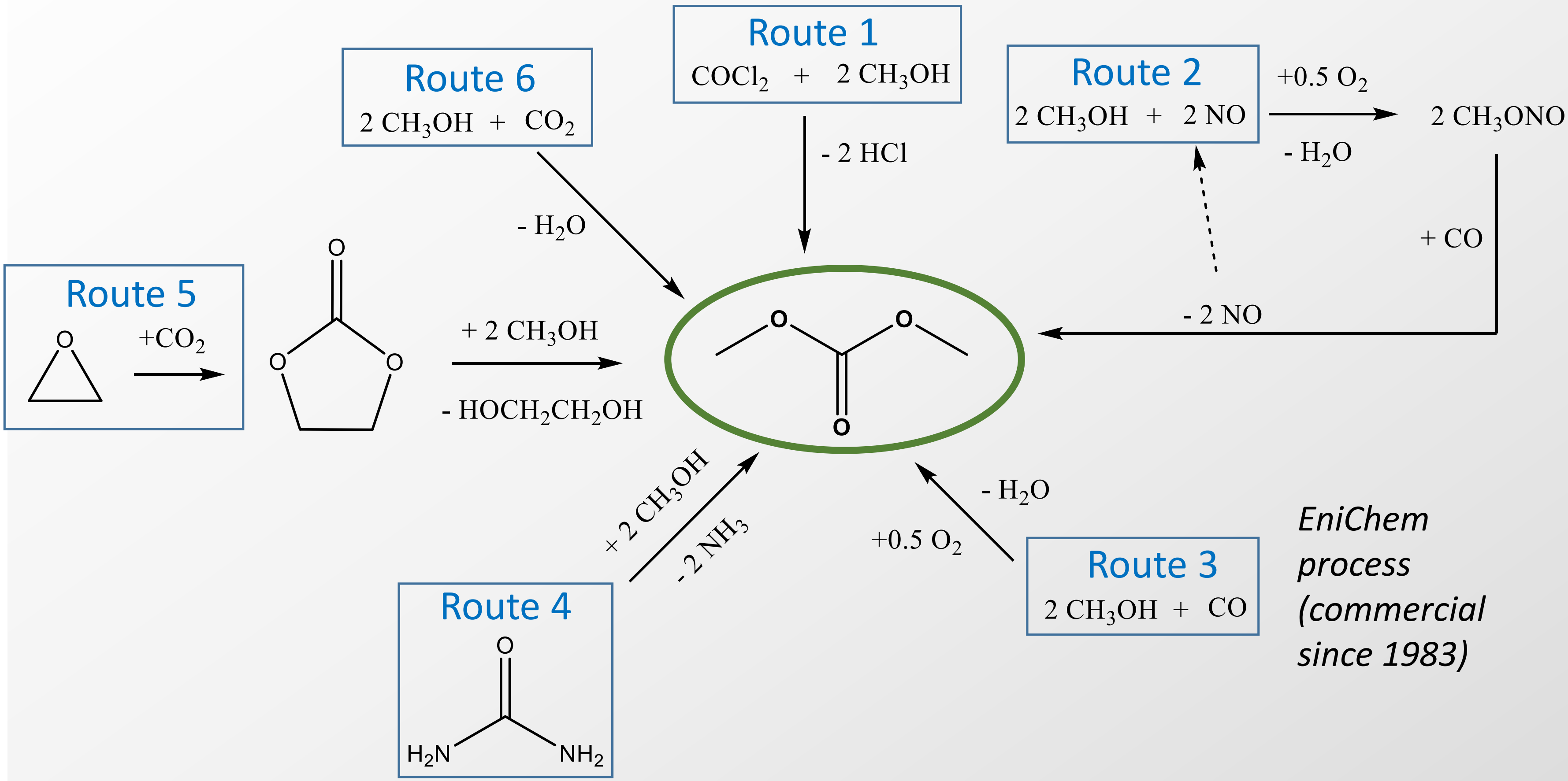
Comparing alternative routes to dimethyl carbonate

Dimethyl carbonate production

- Replacement of hazardous chemicals
  - Phosgene (5-6 Mio tons/yr)
    - Use burdened by growing safety measures for manufacturing, transportation & storage
    - Growing disposal costs
    - Synthesis requires hazardous chlorine
    - Toxic
    - Generates chlorinated by-products
    - Often requires halogenated solvents
  - Toxic methylating agents
    - CH_3Cl
    - Me_2SO4
- Green solvent (non toxic, biodegradable)

Dimethyl carbonate production

Alternative routes



EniChem process (commercial since 1983)

Adapted from:
Monteiro et al., Clean Techn Environ Policy (2009) 11:209–214

Dimethyl carbonate production
Alternative routes

- Route 1: DMC and coproduction of HCl from methanol and phosgene
- Route 2: Methyl nitrite from methanol and NO, followed by production of DMC, CO and recovering of NO
- Route 3: DMC and water from CO and methanol
- Route 4: DMC and NH_3 from urea and methanol (urea production involves CO_2 sequestration)
- Route 5: DMC and ethylene glycol from ethylene oxide and CO_2
- Route 6: DMC and water from CO_2 and methanol

DMC: economical ranking of alternative routes

- Economical ranking based on total conversion of reactants to products and 100% selectivity
- Profit potential *PP* for each route *j* calculated based on stoichiometric factors ($\nu_{j,i}$) of each reactant or product *i* and raw material prices

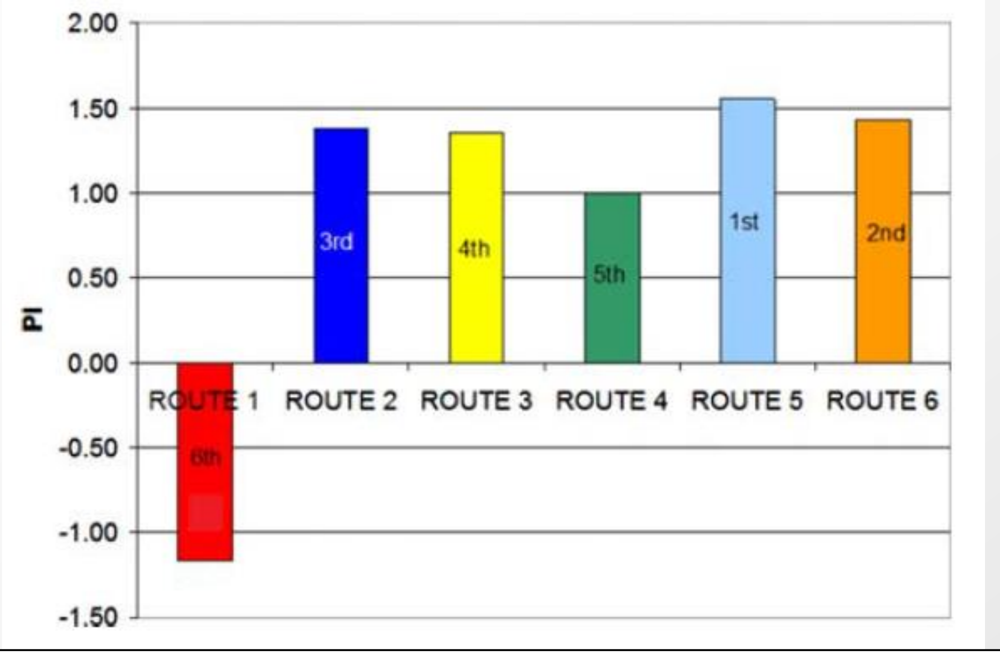
$$PP_j = \sum_{i=1}^{n} \nu_{j,i} P_i$$

- Profit index *PI* for each route *j* evaluated relatively to route 4

$$PI_j = \frac{PP_j}{PP_4}$$

Chemical	**Price (US$/mol)**	**Source**
Hydrochloric acid	0.00342	Icis Pricing
Ammonium	0.00496	Icis Pricing
Carbon credits	0.00084	Chicago Climate Exchange
Dimethyl carbonate	0.10810	Indian Chemicals
Ethylene Glycol	0.06238	Icis Pricing
Phosgene	0.16571	Innovation Group
Methanol	0.01047	Icis Pricing
Carbon monoxide	0.00140	Praxair, Linde Gas
Ethylene oxide	0.05487	Icis Pricing
Nitric oxide	0.00150	Praxair, Linde Gas
Oxygen	0.00477	Praxair
Urea	0.02019	Icis Pricing

DMC: economical ranking of alternative routes



- Route 1: DMC and HCl from methanol and phosgene
- Route 2: methyl nitrite from methanol and NO, followed by DMC, CO and recovery of NO
- Route 3: DMC and water from CO and methanol
- **Route 4:** DMC and NH_3 from urea and methanol (urea production involves CO_2 sequestration)
- Route 5: DMC and ethylene glycol from ethylene oxide and CO_2
- Route 6: DMC and water from CO_2 and methanol

- Profit index (PI) decreases as follows: 5 > 6 > 2 > 3 > 4 >> 1

DMC: toxicity ranking of alternative routes

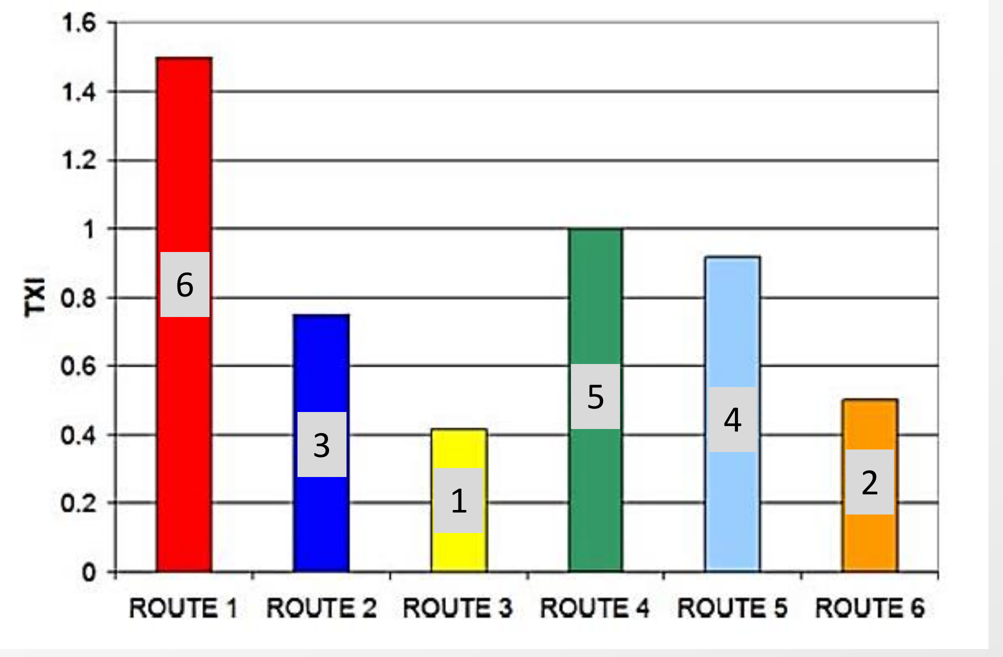
- Toxicity *TX* for each route *j* calculated based on the sum of toxicity of each chemical *i*

$$TX_j = \sum_{i=1}^{n} tx_{j,i}$$

- Toxicity index *TXI* for each route *j* evaluated relatively to route 4

$$TXI_j = \frac{TX_j}{TX_4}$$

DMC: toxicity ranking of alternative routes

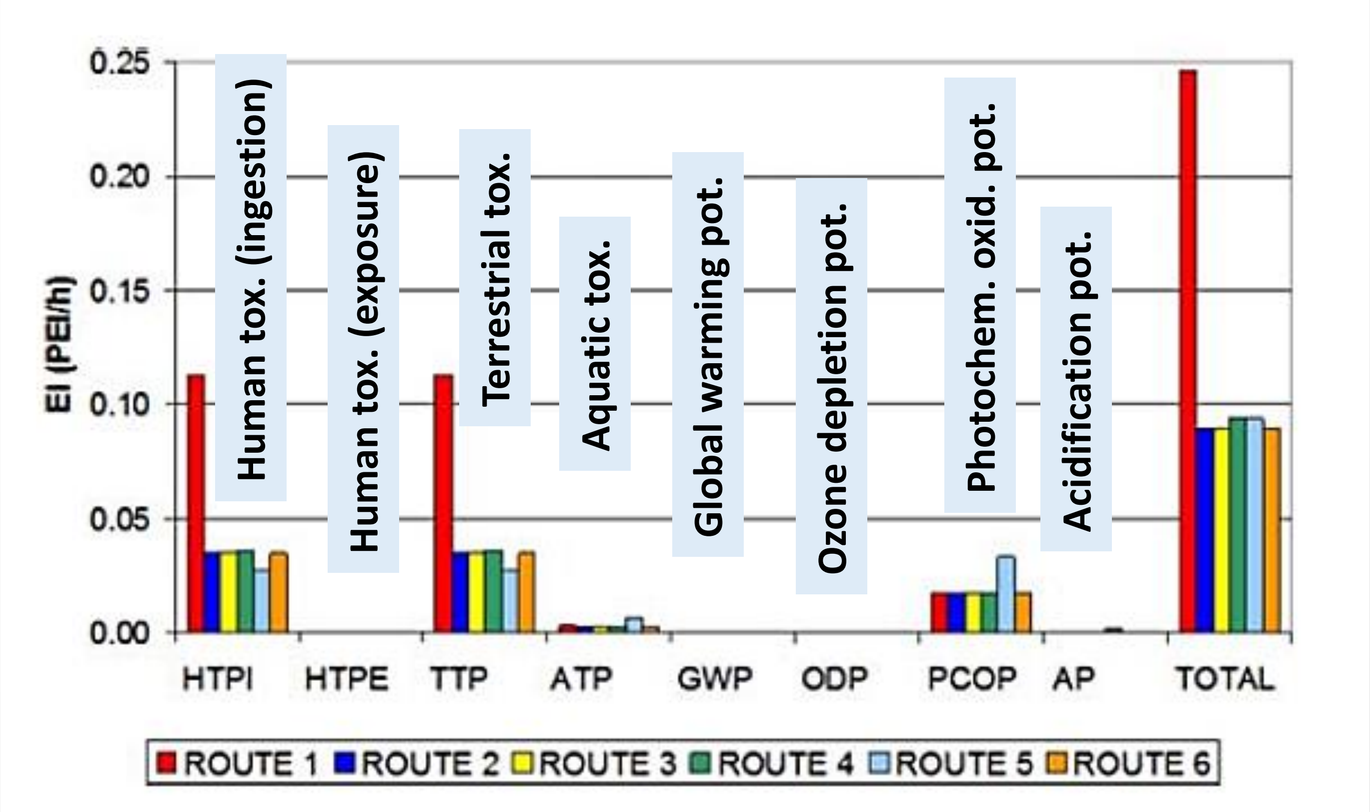


- Route 1: DMC and HCl from methanol and phosgene
- Route 2: methyl nitrite from methanol and NO, followed by DMC, CO and recovery of NO
- Route 3: DMC and water from CO and methanol
- **Route 4:** DMC and NH_3 from urea and methanol (urea production involves CO_2 sequestration)
- Route 5: DMC and ethylene glycol from ethylene oxide and CO_2
- Route 6: DMC and water from CO_2 and methanol

- Toxicity index (TXI) decreases as follows: 1 > 4 > 5 > 2 > 6 > 3

DMC: environmental ranking of alternative routes

- Evaluation of Environmental Index *EI* of route *j* (WAR* software, no weighing)
- Basis: product and reactant flows of 1 kg/h



- Environmental index (EI) decreases as follows: 1 > 4, 5 > 2, 3, 6

* Waste reduction algorithm

PEI: Potential environmental impact

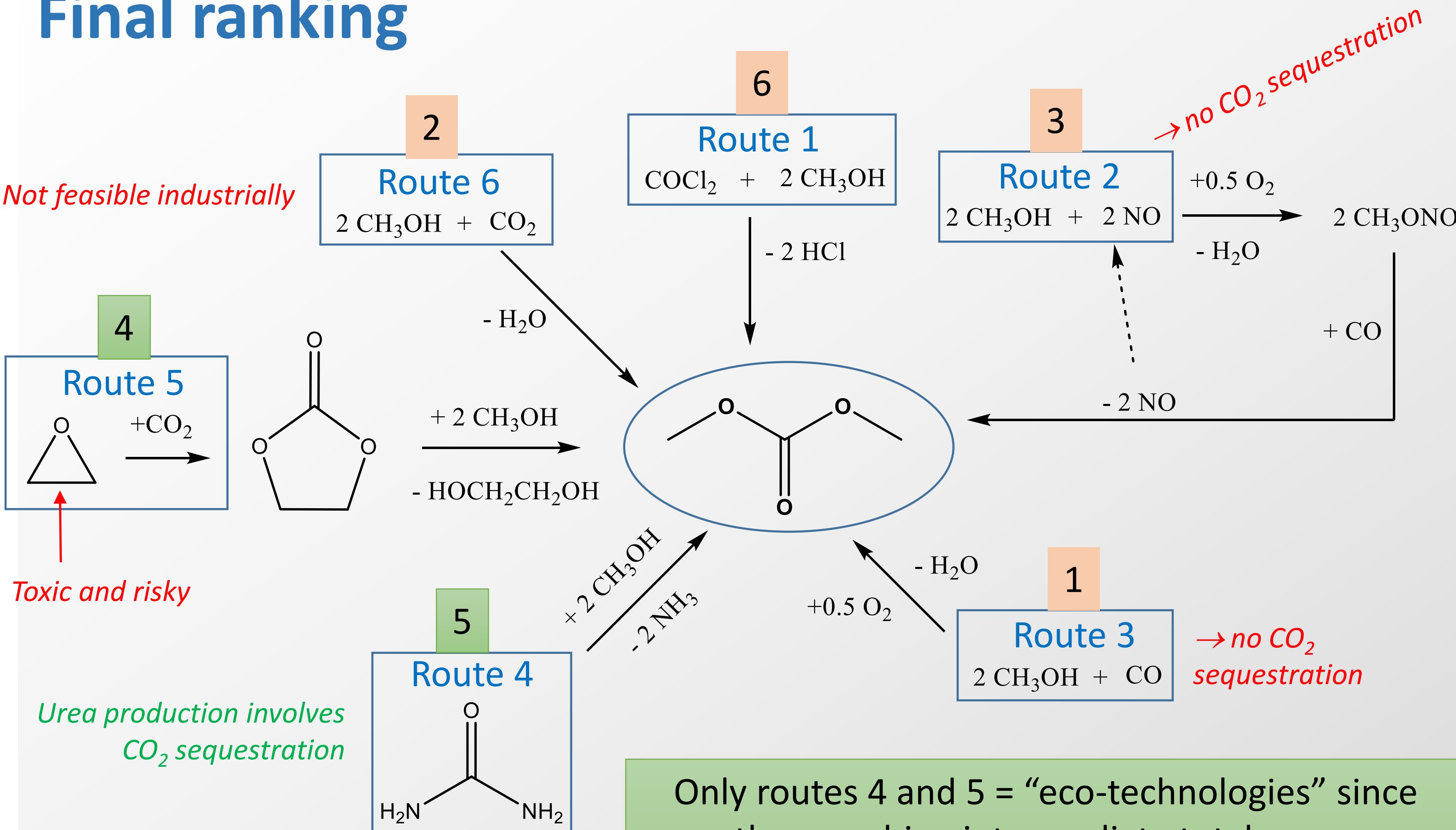
DMC: overall ranking of alternative routes

- Total score of route *j* is an **aggregated metric** based on toxicity, environmental impact and profitability (low value desired)

$$Score_j = \frac{TX_j - TX_{min}}{TX_{max} - TX_{min}} + \frac{EI_j - EI_{min}}{EI_{max} - EI_{min}} + \frac{PP_{max} - PP_j}{PP_{max} - PP_{min}}$$

Route	$\frac{TX_j - TX_{min}}{TX_{max} - TX_{min}}$	$\frac{EI_j - EI_{min}}{EI_{max} - EI_{min}}$	$\frac{PP_{max} - PP_j}{PP_{max} - PP_{min}}$	Total score	Final ranking
1	1.00	1.00	1.00	3.00	LAST
2	0.31	0.00	0.06	0.37	3rd
3	0.00	0.00	0.07	0.07	FIRST
4	0.54	0.03	0.20	0.77	5th
5	0.46	0.03	0.00	0.49	4th
6	0.08	0.00	0.04	0.12	2nd

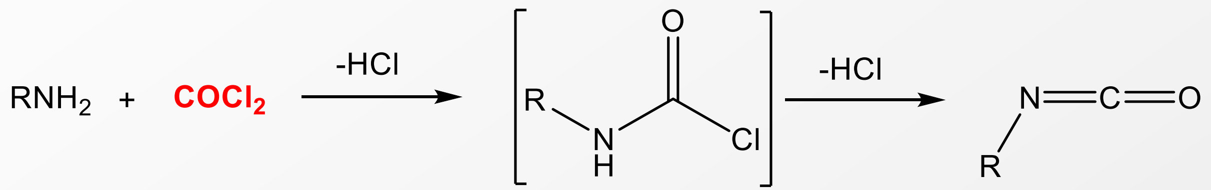
Dimethyl carbonate production
Final ranking

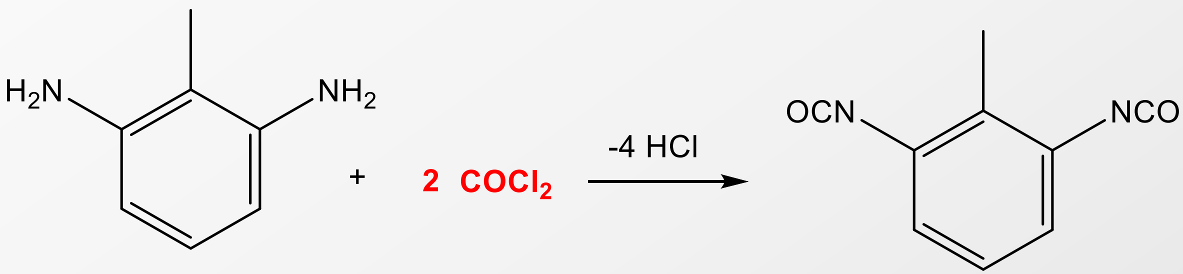


Only routes 4 and 5 = “eco-technologies” since they combine intermediate total score, sequestration potential and industrial feasibility

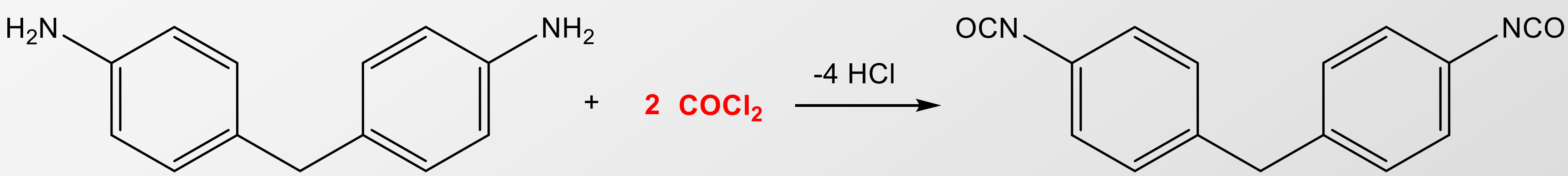
DMC as phosgene replacement

Phosgene uses (isocyanates)





2,6-TDI (polyurethanes, 2.5 Mio tons/yr)



4,4'-MDI (polyurethanes, 7.5 Mio tons/yr)

DMC as a green reagent

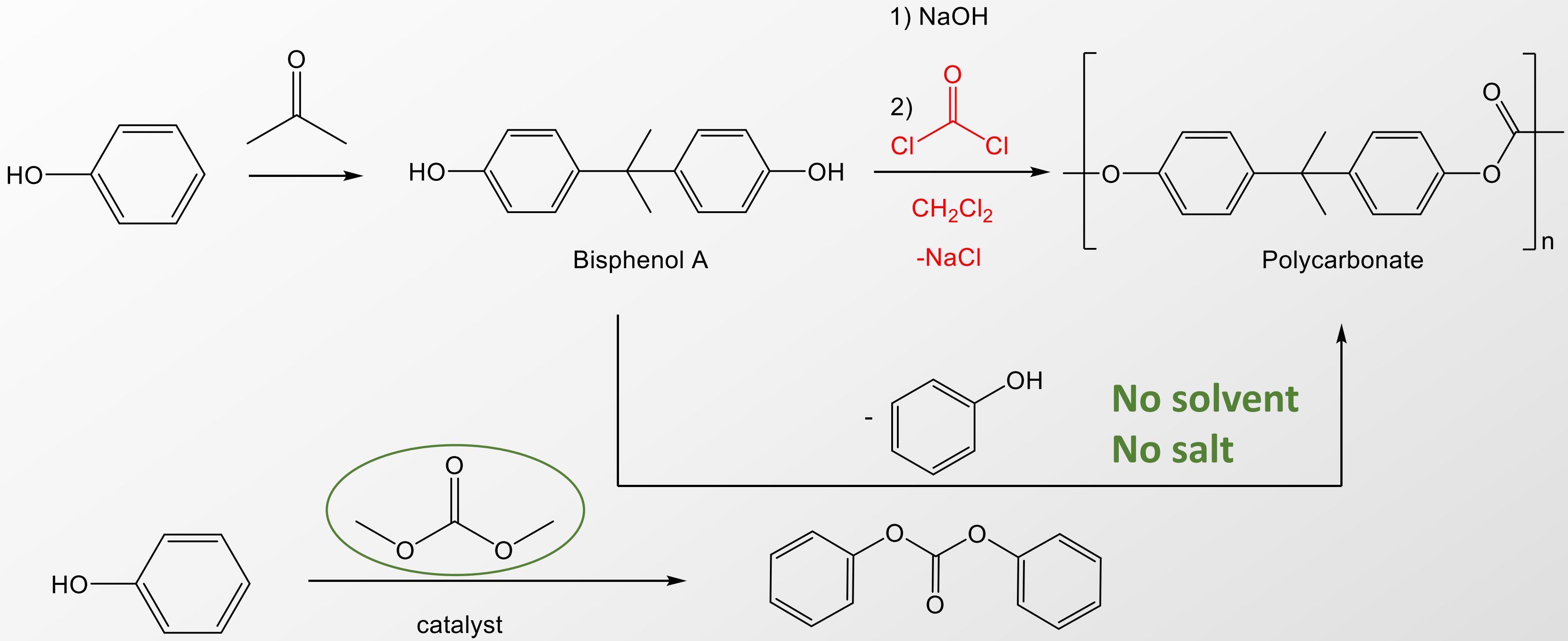
Phosgene or dimethyl sulfate replacement

- ✓ Nontoxic
- ✓ Can be produced by a clean process
- ✓ Biodegradable
- ✓ Reacts in presence of catalytic amount of base (no salts as by-products)

Phosgene or dimethyl sulfate	DMC
Dangerous reagent	Harmless reagent
Use of solvent	No solvent
Waste water treatment	No waste water
NaOH consumption	Base is catalytic
By-products: NaCl, Na_2SO_4	By-products: MeOH, CO_2
Exothermic	Slightly or not exothermic

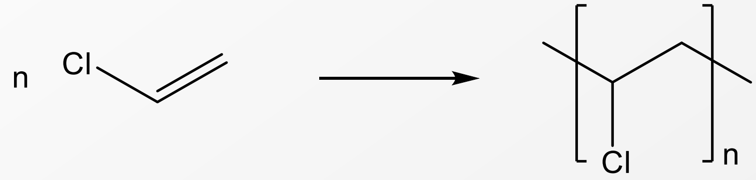
DMC as phosgene replacement

Aromatic polycarbonates from melt-polymerization

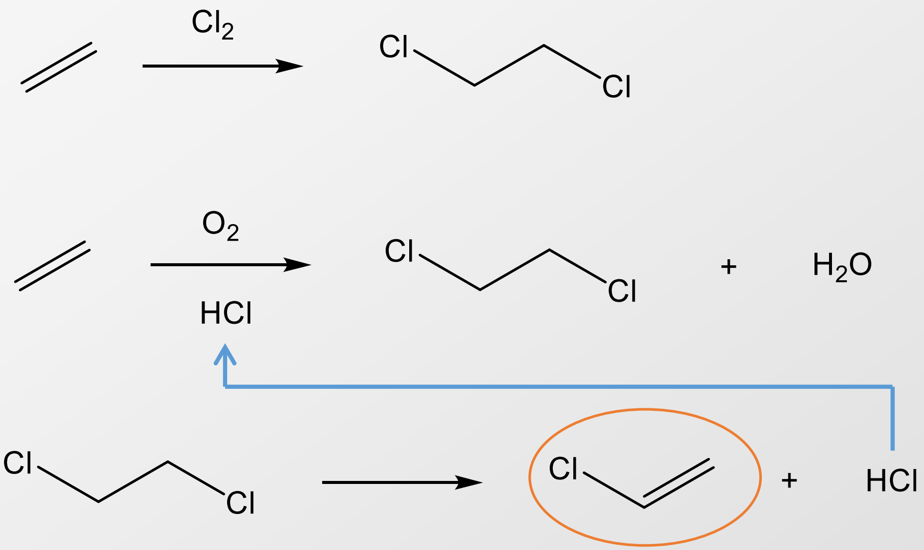


LCA example
PVC production and recycling in China

PVC



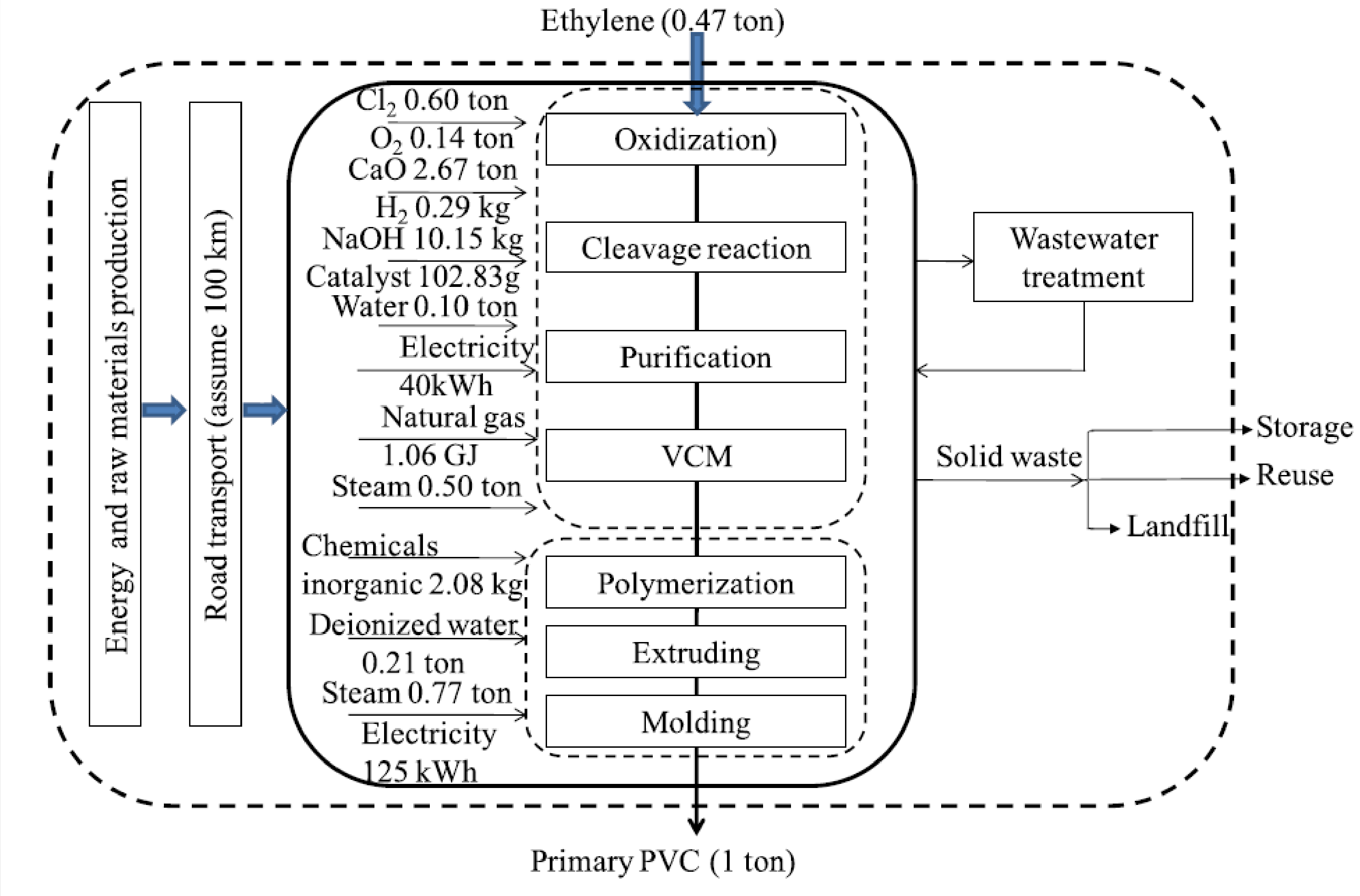
- Poly(vinyl chloride)
- Used e.g. for pipes, cables and various construction materials
- Third most widely consumed plastic (~40 Mio tons)
- ~15 Mio tons produced in China in 2013
- Study conducted to investigate the environmental impact generated from PVC industry
- It includes LCA of producing and recycling PVC



VCM

Primary PVC production

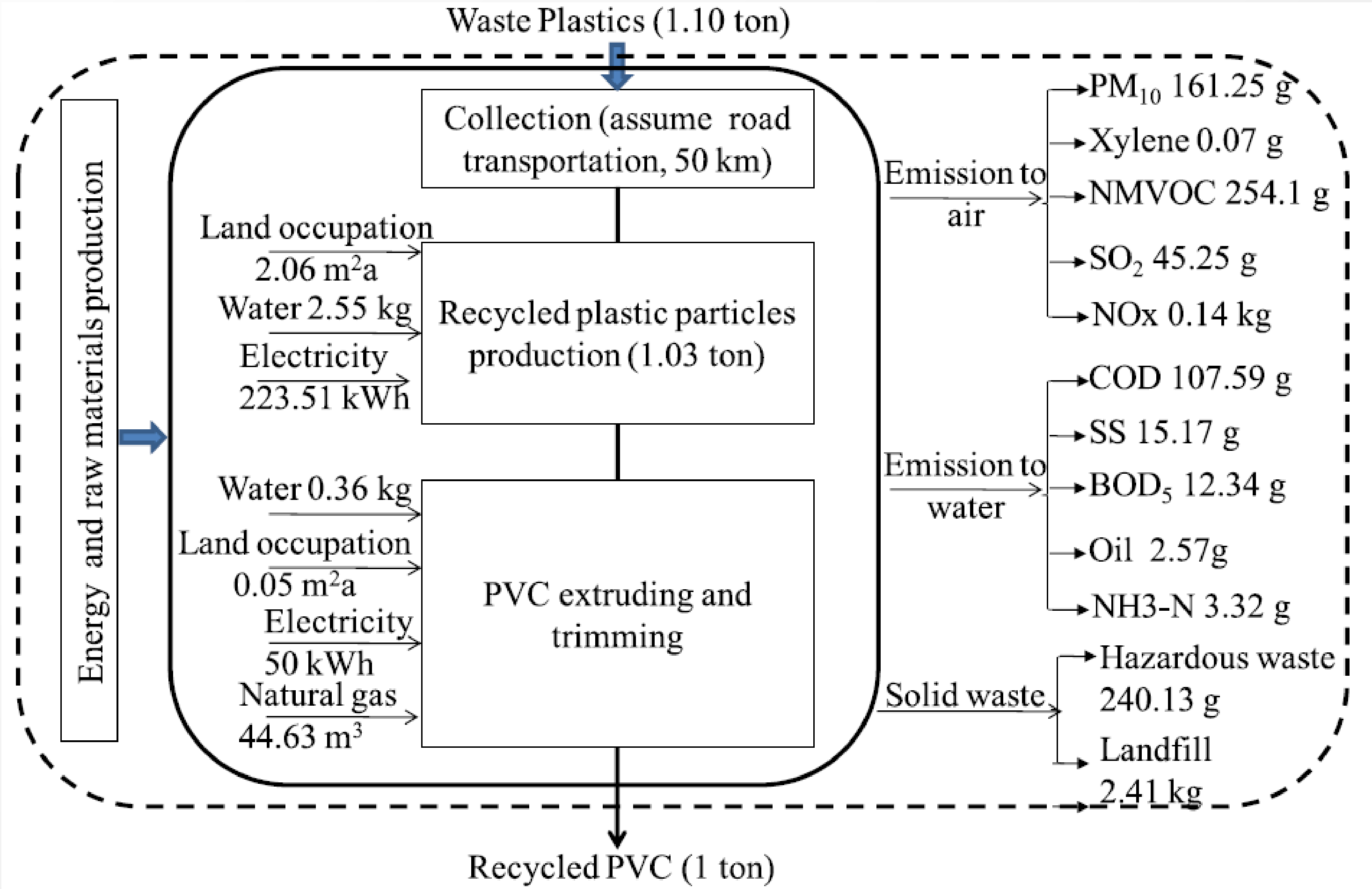
System boundaries with I/O



Ye et al., Journal of Cleaner Production 142 (2017) 2965-2972

PVC recycling

System boundaries with I/O



COD: chemical oxygen demand, BOD: biological oxygen demand, SS: suspended solids, NMVOC: non-methane VOC

Life cycle inventory (LCI)

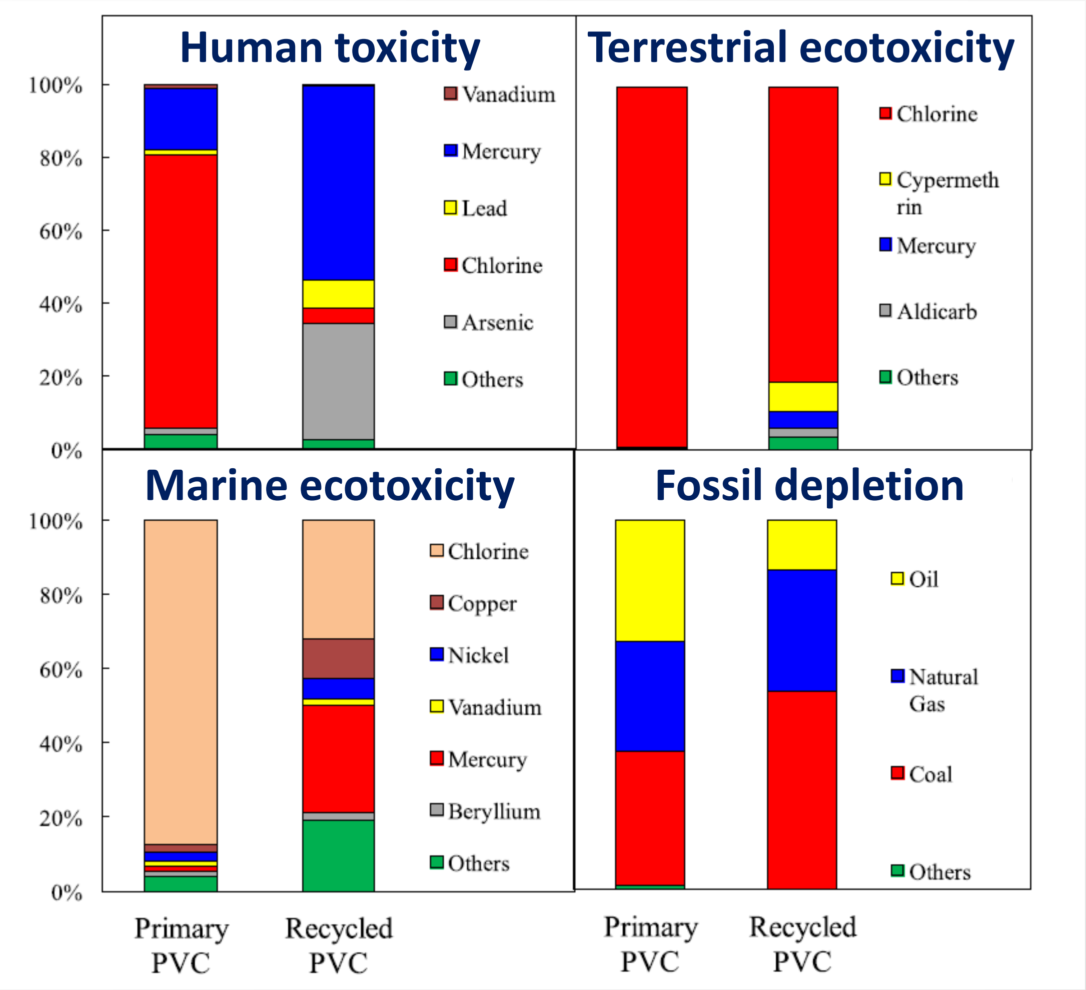
	Categories	Unit	Primary PVC	Recycled PVC
Raw materials	Ethylene	ton	0.47	—
	Waste Plastics	ton	—	1.10
	Catalyst	g	2.18×10^3	—
	Cl_2	ton	0.60	—
	O_2	ton	0.14	—
	CaO	g	26.73	—
	H_2	kg	0.29	—
	NaOH	kg	10.15	—
	Deionized water	ton	0.21	—
	Water	kg	5.84×10^3	2.91
Energy consumption	Electricity	kWh	165.00	273.51
	Natural gas	m^3	29.61	44.63
	Occupation	m^2a	0.08	2.11
	Steam	ton	1.27	—
Air emissions	SO_2	kg	0.43	0.04
	NOx	kg	0.43	0.14
	Particulates	kg	0.21	0.16
	Cl_2	mg	93.28	—
	HCl	mg	2.33	—
	VCM	mg	6.02	—
	Xylene	g	—	0.07
	NMVOC	kg	—	0.25
Emissions to water	SS	g	9.13	15.17
	BOD_5	g	9.35	12.34
	COD	g	48.91	107.59
	Hg	mg	0.56	—
	Chloride	mg	38.87	—
	Oil	g	—	2.57
	NH_3	g	—	3.32
Waste to treatment	Industrial Hazardous Waste	g	—	240.13
	Landfill	g	19.43	2.41×10^3
	Wastewater	ton	1.46	0.36

Life cycle impact assessment (LCIA)

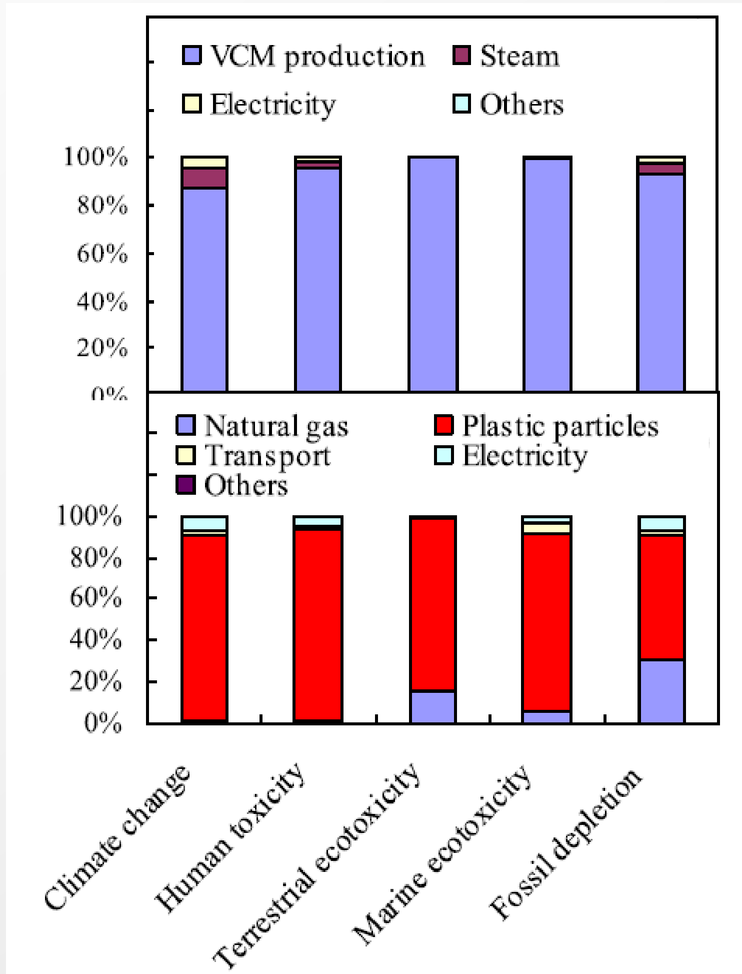
Categories	Unit	Primary PVC	Recycled PVC
		Value	Value
Climate change	kg CO_2 eq	2.82×10^3	646.81
Ozone depletion	kg CFC-11 eq	9.30×10^{-5}	7.17×10^{-6}
Terrestrial acidification	kg SO_2 eq	9.59	1.82
Freshwater eutrophication	kg P eq	0.03	1.71×10^{-3}
Marine eutrophication	kg N eq	0.48	0.08
Human toxicity	kg 1,4-DB eq	428.42	59.17
Photochemical oxidant formation	kg NMVOC	12.29	2.19
Particulate matter formation	kg PM_{10} eq	3.58	0.84
Terrestrial ecotoxicity	kg 1,4-DB eq	14.99	0.13
Freshwater ecotoxicity	kg 1,4-DB eq	0.76	0.03
Marine ecotoxicity	kg 1,4-DB eq	6.29	0.12
Ionising radiation	kBq U235 eq	110.41	2.86
Agricultural land occupation	m^2a	10.34	5.28
Urban land occupation	m^2a	7.20	2.53
Natural land transformation	m^2	0.17	0.03
Water depletion	m^3	57.52	3.37
Metal depletion	kg Fe eq	48.48	3.38
Fossil depletion	kg oil eq	1.12×10^3	138.09

Primary PVC has higher environmental impact scores in each category

Main contributors



Main process contributing to significantly affected categories



Primary PVC

Recycled PVC

Conclusions

- Recycled PVC production more environmental-friendly compared with primary PVC production.
- Notable impacts on terrestrial ecotoxicity, human toxicity, marine ecotoxicity, and fossil depletion observed.
- Primary PVC has a greater impact than recycled PVC in most categories except for agricultural land occupation
- Limitations of study: PVC production varies in terms of technology, material input, and process control in China → These two cases cannot fully reflect the Chinese levels of primary and recycled PVC productions

Roles of green chemistry and engineering in LCA

Roles of green chemistry and engineering in LCA

Green chemistry can lead to improvements at all stages of product/process life cycle

Energy / environment / materials

Materials aquisition and input

- Alternative feedstocks
- Alternatives to current mining (electrochemistry)
- Alternatives to harvesting
- Auxiliary substances
- Bio-based and renewable
- Eliminate impacts of material acquisition
- Eliminate imports
- Energy instead of material
- More innocuous/less toxic solvents
- Waste as inputs

Manufacturing, processing and formulation

- Atom economy
- Catalysis
- Design of safer chemical rules
- Energy minimized
- Minimized solvents in formulation
- Reagents hazards reduced

Packaging and distribution

- Efficient production conception minimizes amount of packaging
- Incorporate packaging made of same material as product
- Lower transportation costs by form of product
- Packaging not required

Product use

- Design requires low/no energy
- Use of product neither consumes material nor generates waste

EOL: recycling, reuse and disposal

- Designed to biodegrade in the environment
- Highest entropy products made most durable
- Materials/polymers/ plastics transform to virgin materials

Adapted from Anastas & Lankey, Green Chemistry, 2000, 2, 289–295

Roles of green chemistry and engineering in LCA
Example: materials acquisition and input

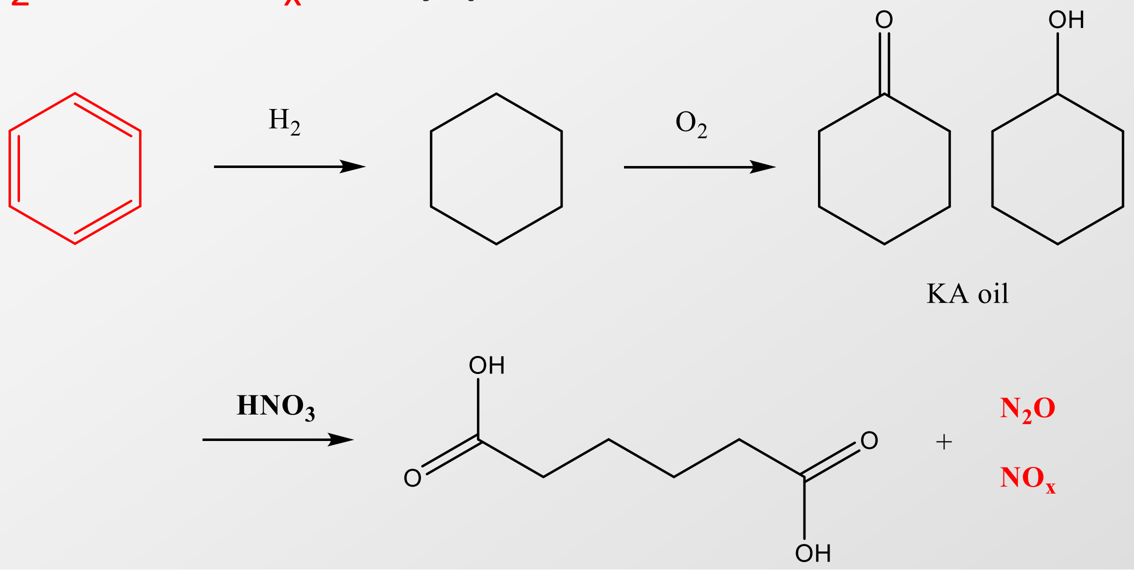
- Some considerations concerning materials acquisition and input:
  - Methods used to obtain starting materials (mining, refining, agriculture,…) should have minimum impact on the natural environment
  - The material inputs over the life cycle should be of minimum toxicity
  - Starting materials should be renewable rather than depleting wherever possible.
  - When possible, the starting materials for a process should be the 'waste' from another process.

Anastas and Lankey, Green Chemistry, 2000, **2**, 289–295

Roles of green chemistry and engineering in LCA
Example: materials acquisition and input

Example: adipic acid synthesis

- Starting material for Nylon 6,6 (~2 mio T/y)
- Classic route to adipic acid from (non sustainable) petroleum-derived benzene
- Oxidation of intermediate cyclohexanone/ol mix using nitric acid → N_2O and NO_x as by-products



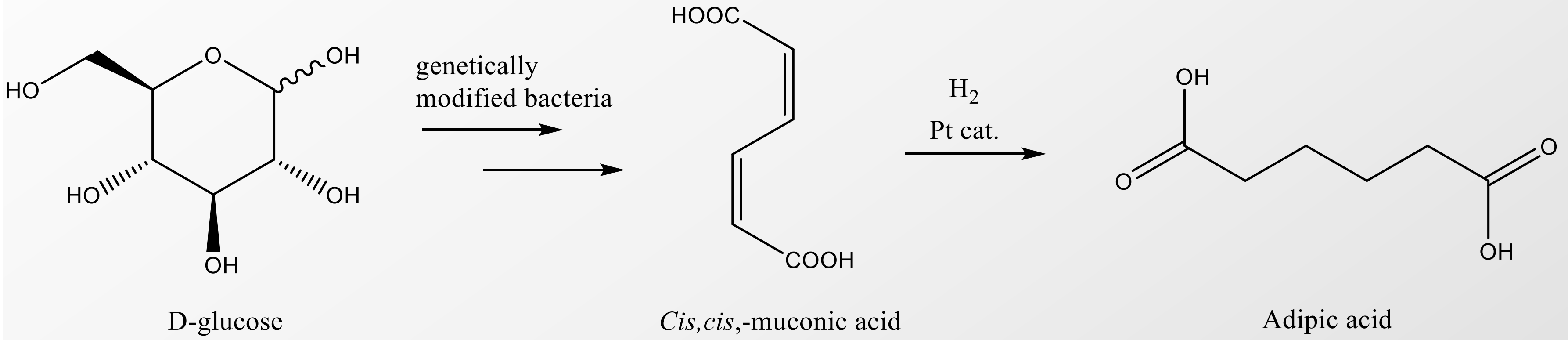
Roles of green chemistry and engineering in LCA
Example: materials acquisition and input

Example: adipic acid synthesis

- N_2O responsible for ~10% of annual increase in atmospheric N_2O levels
- Intrinsic contribution (per kg) of N_2O to global warming is 275 times higher than CO_2
- New “green” Draths–Frost synthesis
  - ✓ Renewable feedstock (glucose)
  - ✓ Process materials of little or no toxicity
  - ✓ No more benzene use or N_2O and NO_x emissions

Roles of green chemistry and green engineering in LCA

Draths–Frost process



Niu et al., Biotechnol. Prog., 2002, Vol. 18, No. 2